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Mobilization of a Hydrophobic Organic Compound Using Surfactant for Soil Washing.

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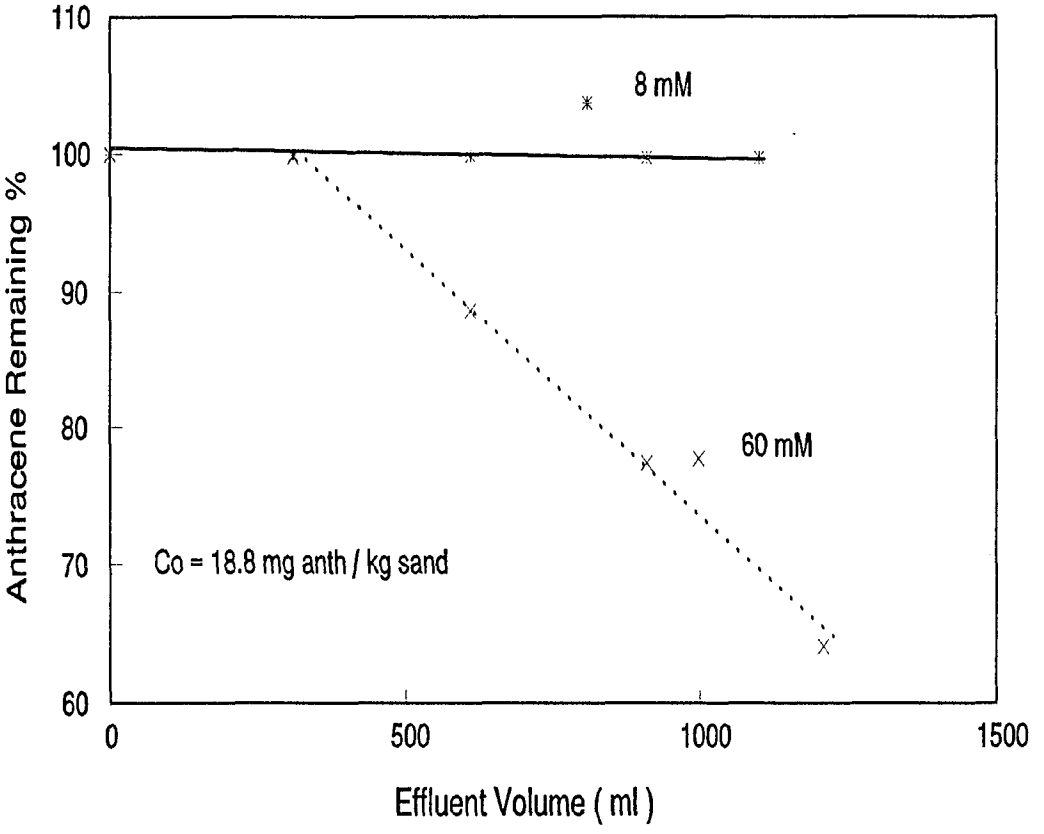

Figure 4.4 Comparison of the effectiveness of 8 mM and 60 mM SDS solution (the experimental setup is in Figure A.2).

no significant change in the solubility of anthracene is observed. To verify the increase in anthracene mobilization from the column experiments, the SDS concentration in the effluent was monitored. The results of this experiment (Figure 4.5) show that a higher anthracene concentration in the effluent is associated with a higher SDS concentration.

Conclusions

Based on the results of this research, the following specific conclusions can be drawn:

- The solubility of anthracene is a linear function of surfactant concentration above the CMC level.
- Anthracene cannot be effectively removed by water or surfactant solution at a concentration less than or equal to the CMC.
- SDS, an anionic surfactant, can be successfully used to solubilize hydrophobic organic compounds, such as anthracene, from saturated sandy environments under dynamic conditions.

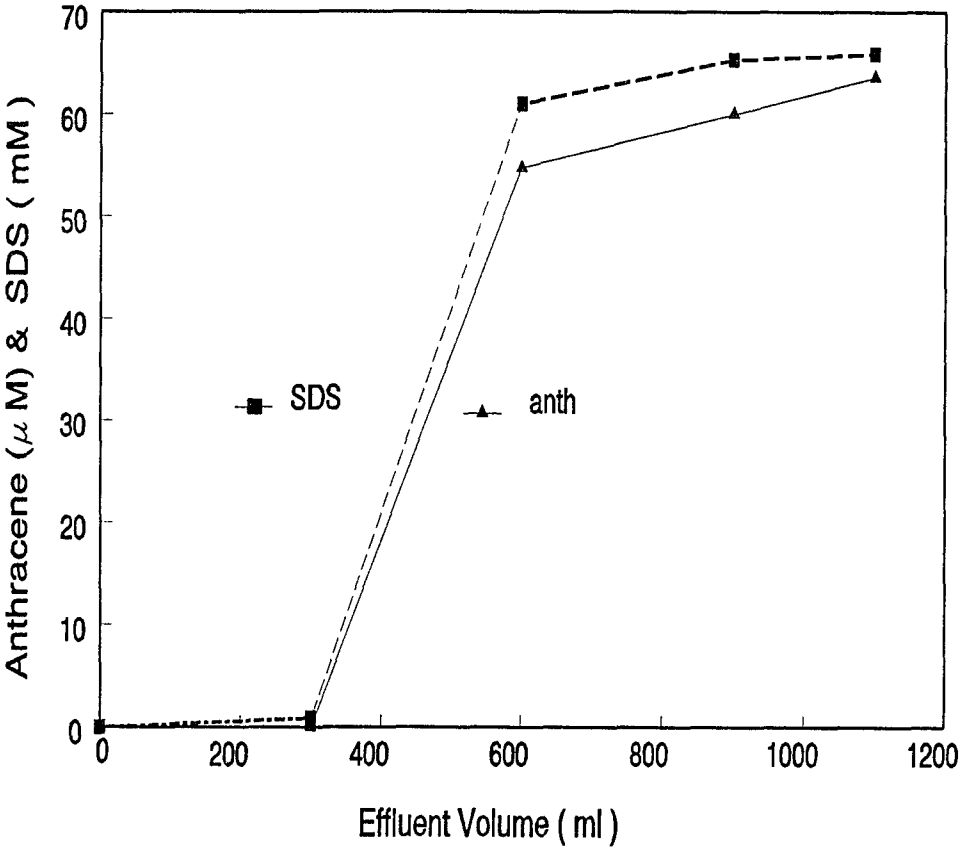

Figure 4.5 Anthracene and SDS concentration change in the column effluent (the experimental setup is in Figure A.2 and the pore velocity is 0.364 cm/min).

CHAPTER 5
LABORATORY INVESTIGATION AND MODELING OF ANTHRACENE REMOVAL FROM CONTAMINATED SAND COLUMNS BY SURFACTANT SOLUBILIZATION

Introduction

Various organic chemicals will be released into the underground environment through spills, leaking containers, and waste-oil processing. Groundwater pumping and treatment is a major non-source control remediation technology selection (EPA, 1990). In a subsurface situation of slightly hydrophilic and hydrophobic organic compounds contamination, pumping groundwater alone may take decades to achieve a significant reduction of these organic contaminants. Surfactant soil washing technology shows great potential as an *in-situ* remedial action plan to remove hydrophobic organic compounds because it mobilizes contaminants by increasing their aqueous solubility.

The purposes of this research are to evaluate the potential of *in-situ* soil washing by surfactants for contaminated sandy soil and to develop a mathematical model for the process of soil washing based on laboratory scale experimental results. Anthracene was selected as the model hydrophobic organic compound because it is nearly insoluble in water (0.073 mg/l) and it has been recommended as the target contaminant by Superfund Standard Analytical Reference Matrix (Esposito et al., 1988). Sodium Dodecylsulfate (SDS) was chosen as the representative surfactant because it is well investigated (Rosen, 1989; Vold and Vold, 1983) and biodegradable (Swisher, 1987). SDS has been demonstrated to greatly increase the solubility of

anthracene and the solubility of anthracene was noted to be a linear function of SDS concentration above the critical micelle concentration (CMC) of SDS (Liu and Roy, 1992).

Materials and Methods

Chemicals

Anthracene (99%), was purchased from Sigma Chemical Co. (St. Louis, MO). Anthracene's ($C_{14}H_{10}$) molecular weight is 178.24 and boiling point is 342°C. The solubility of anthracene in water is 0.073 mg/l (Dzombak and Luthy, 1984). High purity (99.5%) reagent grade Sodium Dodecylsulfate (SDS) was obtained from Life Technologies, Inc. (Gaithersburg, MD). The structure of SDS is CH_3-$(CH_2)_{11}$-SO_4^- Na^+ and its molecular weight is 288.38. The critical micellar concentration (CMC) of SDS is 8.0 mM (Vold and Vold, 1983).

Sand and Soil

A fine sand sample was obtained from Industrial Sand Co. (Baton Rouge, LA). Sieve analysis performed on the sand sample showed that d_{10} = 0.11 mm and the uniformity coefficient (d_{60}/d_{10}) was 1.76. Since the uniformity coefficient was less than 2.0, the sand sample was classified as a uniform fine sand. The organic content of the sample was measured to be approximately 0%.

A soil sample was obtained from the subsoil of a lot adjacent to the Louisiana State University greenhouse. The soil sample was air dried, and pulverized particles larger than 2 mm were discarded. The soil is a silty clay loam. It has low organic

content and mineral analysis shows that the soil sample contains a small quantity of Montmorillonite.

Anthracene Measurement

Anthracene analysis was performed using either a Diode Array UV/V Spectrophotometer (Model 8452A, Hewlett Packard, Avondale, PA) or a HPLC (Series 1050, Hewlett Packard, Avondale, PA). The absorbance wave range of 252 to 254 nm was used in all UV/V spectrophotometer analyses of anthracene. For HPLC, a pre-packed column, Envirosep-pp 125×3.2 (Phenomenex Co., Torrance, CA) was used, and the general method provided by the column manufacturer was used. All soil washing samples for analysis of anthracene were centrifuged for 7 minutes at 14,000 rpm (Model 5415, Brinkmann Instruments Inc., Westburg, NY) before measurement and if necessary were then further filtered through a 0.45 μm, teflon syringe filter (Nalge Co., Rochester, NY).

Batch Experiment for the Comparison of SDS Loss

20 or 40 grams of sand and air-dried soil were placed in glass bottles containing 50 ml of SDS solution. The glass bottles were shaken in a rotary shaker for 24 hours. The supernatant was collected, centrifuged (Brinkmann Centrifuge Model 5415) at 14,000 rpm for 10 minutes, and then analyzed. Samples were taken from duplicated or triplicated runs, and a blank was used as a control to account for the adsorption of the chemical on the glass surface.

Batch Experiment for the Comparison of Anthracene Adsorption

Anthracene adsorption on sand and soil were conducted in 30 mM SDS solution. First 30 mM SDS solution with extra anthracene crystals was stirred for 48 hours to reach the saturation solubility of anthracene. Then the solution was allowed to stand over night to insure that the solution was not over saturated. It was then filtered through a 0.45 μm membrane to remove the extra anthracene solid. The filtrate was diluted into a series of different anthracene concentration using the pure SDS solution (30 mM). Soil and sand were added to these solutions separately and these suspensions were shaken in a shaker at 25°C. The weight ratio of liquid to soil was 10 to 1 and the containers were 250 ml polycarbonate centrifuge bottles (International Equipment Company, Needham Hights, MA). After 88 hours of shaking these suspensions were centrifuged at 10000 rpm for 15 min (B22 centrifuge, 875 rotor, International Equipment Company, Needham Hights, MA), the supernatant was collected and analyzed. For each concentration, a blank was used as a control to account for the adsorption of anthracene on the wall of the bottle.

Contamination Procedure of Sand

Sand spiking was done by first dissolving anthracene in 200 proof ethyl alcohol (Quantum Chemical Corporation, Tuscola, IL) and then mixing the sand in a rotary tumbler with this solution for 10 minutes. Then the wet mixture of sand was placed in a hood, and the ethyl alcohol was allowed to evaporate. The initial contaminant concentration was determined by extracting anthracene from 5 grams of spiked sand by ethyl alcohol or acetonitrile on a shaker for 4 hours.

Batch Experiment for Contaminated Sand

60 mM SDS solution was used in batch kinetic tests. The flasks contained 100 ml surfactant solution with different amounts of contaminated sand in the range of 1 to 7 grams. The initial anthracene concentration of sand was 188 mg anthracene/kg sand. The flasks were shaken on a rotary shaker. The anthracene concentrations in solution were measured at 3, 10, 30, and 120 minutes and then in 120 minute intervals until 1200 minutes.

In another group test, the range of the amount of contaminated sand were 0.5 to 20 grams and the initial anthracene concentration of sand was 108 mg anthracene/ kg sand. The final anthracene concentration in aqueous phase was measured after 20 hours shaking.

Column Experiments

The column used in the soil washing experiment was stainless steel, 12 in. long and 2.5 in. inside diameter. A filter stone was placed at the bottom of the column, and successive plugs of spiked sand weighing 250 g were packed until each column contained 1600 grams. After a column was packed, 300 ml distilled deionized water was pumped into the column for the purpose of driving air out and saturating the sand. Then surfactant solution or water was pumped continuously at a rate of 300 ml per hour by a pump (Model QG 20, Fluid Metering, Inc., Oyster Bay, NY). The column effluent was collected for organic analysis.

Results and Modeling of Batch Experiments

The loss of SDS on sand or the interaction between sand and SDS has been studied in a batch experiment. To contrast the different SDS adsorption on sand and soil, same amount of sand and soil were used for the test. The results of the experiment presented in Figure 5.1 suggest that the presence of sand up to 40 g/50 ml SDS solution did not result in any loss of surfactant from aqueous phase. On the contrary, the surfactant concentration in the aqueous phase was greatly reduced by the presence of soil. The loss of surfactant is likely due to the interactions such as ion exchange, precipitation, and adsorption (Walker et al., 1978). Therefore, for sand flushing experiment, the reaction term for the loss of SDS in the mass balance equation can be eliminated.

The results of anthracene adsorption on sand and soil in the presence of 30 mM SDS solution are shown in Figure 5.2. Adsorption of anthracene by sand at all levels of initial concentration appears to be insignificant. This negligible adsorption of anthracene by sand could be attributed the low organic content and less surface area for fine sand. However, a clear reduction in the anthracene concentration of aqueous phase was noted for the experiments using soil. Hydrophobic adsorption for compounds such as anthracene is driven not only by the attraction of the compounds to the organic matter in soil, but also by the incompatibility of the non-polar compounds with water (Westall, 1987). The use of surfactant increases the solubility of hydrophobic organic compounds as well as the stability of these compounds in aqueous phase, thereby reducing the incompatibility of anthracene with water.

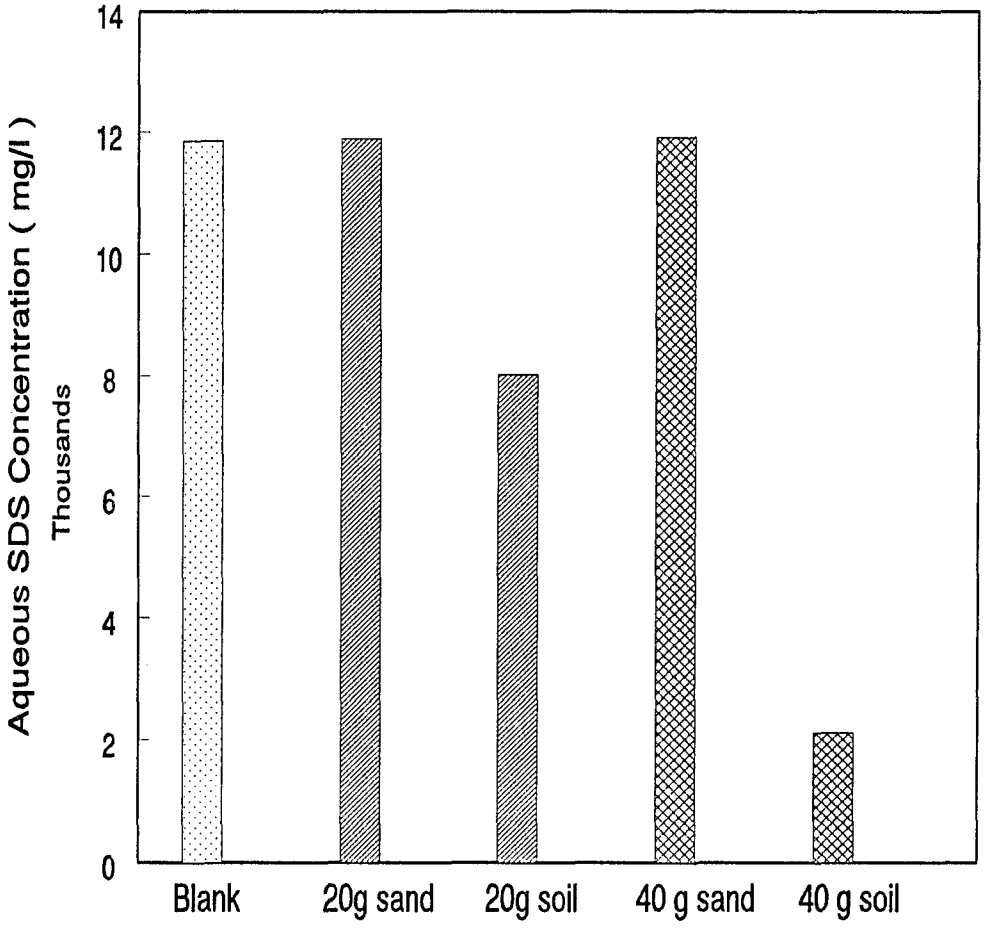

Figure 5.1 Comparison of SDS interaction with sand and soil (50 ml SDS solution + 20 or 40 g of sand or soil).

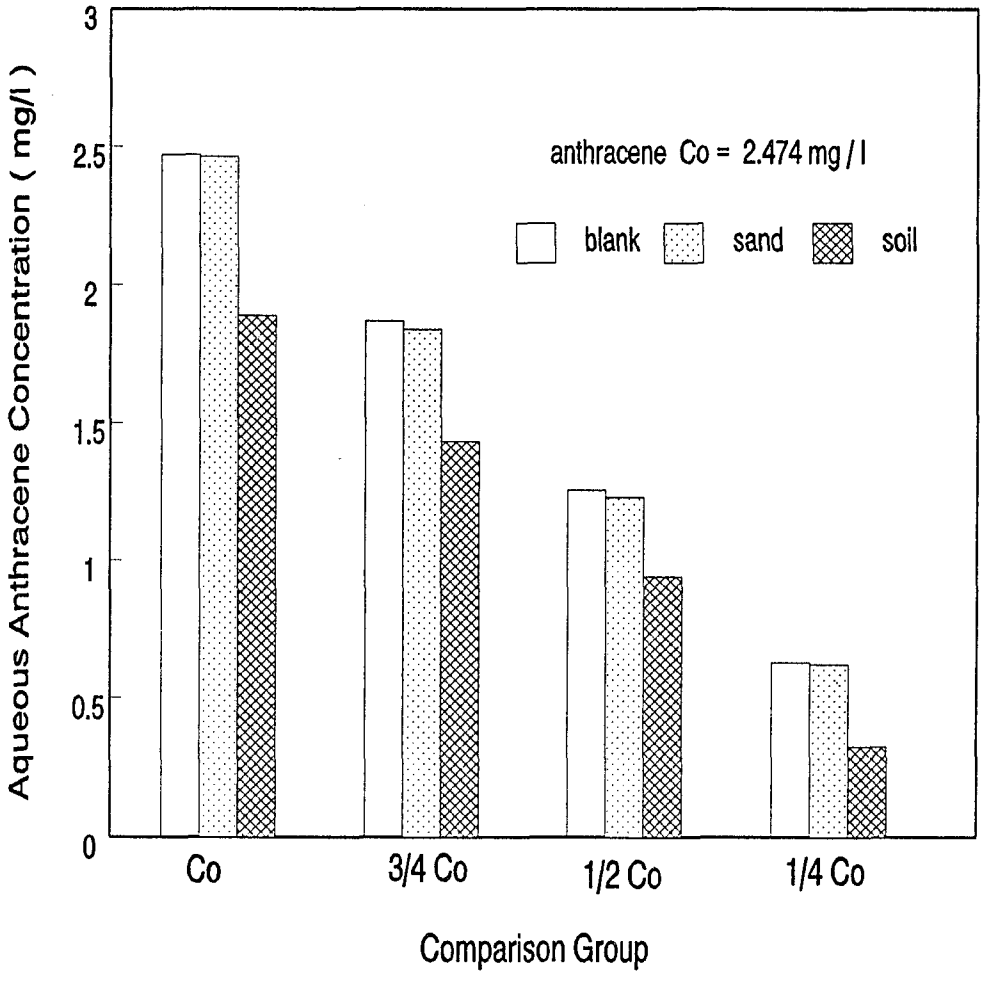

Figure 5.2 Comparison of anthracene adsorption on sand and soil in the presence of SDS (30 mM).

Mobilization of anthracene molecules from sand particles were first studied in nine batch reactors using 0.5 to 20 grams contaminated sand in 100 ml of 60 mM SDS (Figure 5.3). For the reactors containing less than 9 grams of sand, the aqueous anthracene concentration increased linearly in a steep slope with an increase of the contaminated sand amount. For the experiments using sand above 12 grams, the aqueous anthracene concentration reached approximately 10 mg/l which is near the limited solubility of anthracene in 60 mM SDS (11.1 mg/l). Hence, the removal of anthracene from contaminated soil in apparent equilibrium experiment is limited by the solubility of anthracene in SDS solution suggesting that the solubilization is the main mechanism for anthracene removal from contaminated sand.

The kinetics of solubilizing anthracene in the micellar phase of SDS were studied in four batch reactors using 100 ml of 60 mM SDS containing 1, 3, 5 and 7 grams of contaminated sand. The initial anthracene concentration of the sand was 188 mg anthracene/kg sand. The change of anthracene concentration in 60 mM SDS of each reactor as a function of time is presented in Figure 5.4. The change was very rapid during the initial stage, then it declined slowly as the apparent equilibrium was approached. A similar phenomenon was also observed by Jafvert (1991) who reported that phenanthrene desorbed rapidly from sediment soil into SDS solutions in the first 3 hours and reached equilibrium in about 16 hours.

Since the amount remaining in sand particles was a linear function of the concentration in solution, mass balance in a flask was

$$q \times m = q_o \times m - c \times v \qquad (5.1)$$

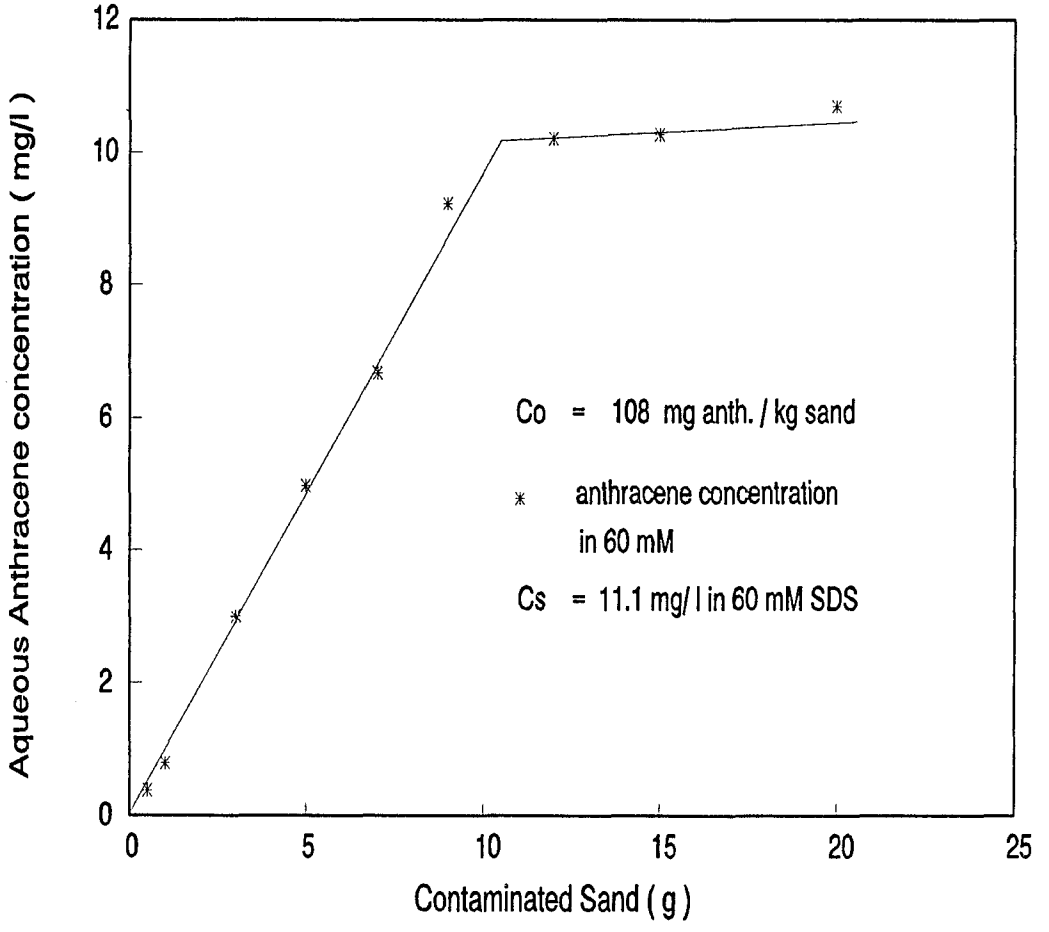

Figure 5.3 Batch experiment of anthracene removal from contaminated sand by 60 mM SDS solution.

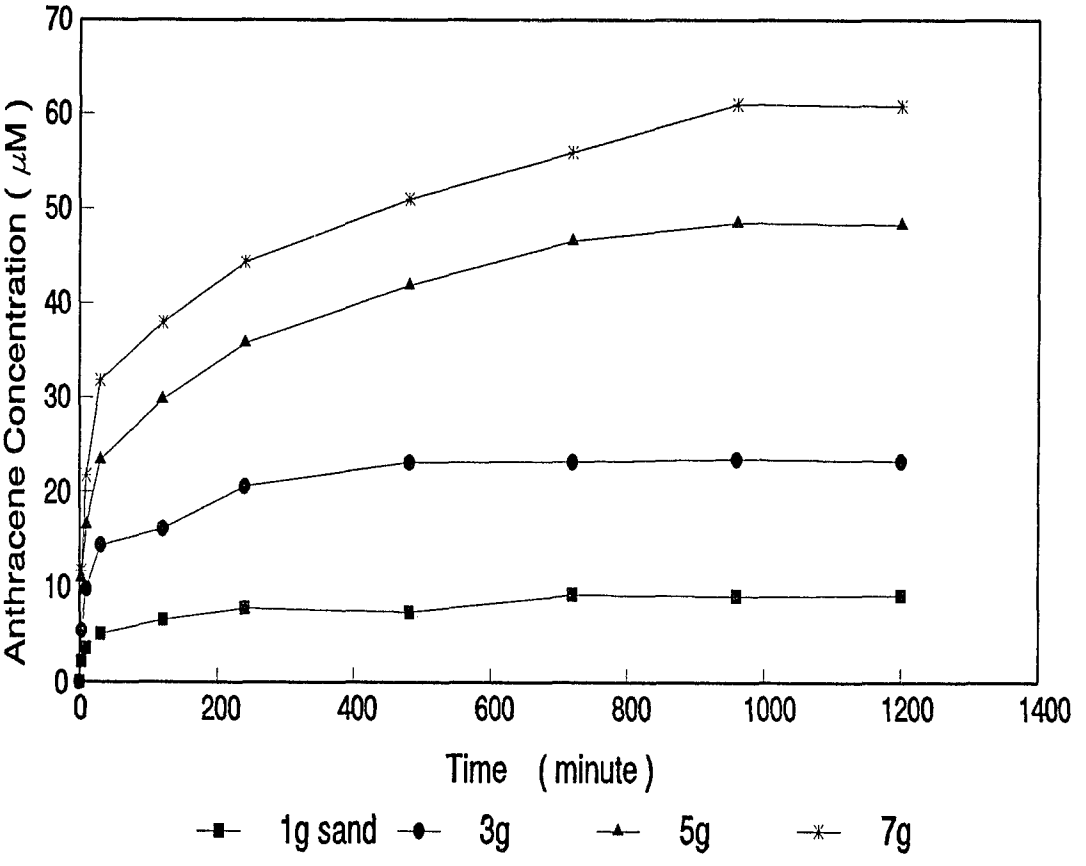

Figure 5.4 The kinetics of anthracene removal from contaminated sand by 60 mM SDS solution.

where m is the weight of sand; v is the volume of solution and q is residual anthracene mass per unit mass of sand. The change of q can be calculated through the change of anthracene concentration in the liquid phase. An attempt was made to fit first and second order rate equations for the experimental data obtained for the surface associated anthracene concentration. It was noted that first and second order rate kinetics did not fit the experimental data well. In view of this, an exponential equation known as the Elovich equation (Low, 1960) has been tried for the data on anthracene solubilization by SDS. The exponential Elovich equation has been used to describe heterogeneous isotopic exchange reactions (Atkinson et al., 1970) and phosphate release and sorption in soils (Chien and Clayton, 1980). The Elovich equation is generally expressed as

$$\frac{dq}{dt} = \alpha \exp (- \beta q) \qquad (5.2)$$

where q is the amount of chemical on the soil at time t, and α and β are constants during any one experiment. For decontamination assuming $q=q_o$ at $t=0$, the integrated form of equation (5.2) becomes

$$q = \frac{1}{\beta} \ln (\alpha \beta t + e^{\beta q_o}). \qquad (5.3)$$

Non-linear regression techniques for the experimental data (q_o=0.188 mg anth/g sand) determined that β=-45.34. Since the second term, $e^{\beta q}$, can be shown to be much smaller than the first term, the second term can be dropped out and the equation (5.3) becomes

$$q = \frac{1}{\beta} \ln(\alpha \beta t) = \frac{1}{\beta} \ln (\alpha \beta) + \frac{1}{\beta} \ln(t) \qquad (5.4)$$

Equation (5.4) is a linear relation between q and ln(t). Applying equation (5.4) to the experimental data, we obtain a straight line (R^2=0.956) on washing of 1, 3, 5 and 7 gram sand samples contaminated with anthracene. The equation of the straight line is

$$q = 0.178 - 0.0213 \ln (t) \qquad (5.5)$$

Experimental observations and a graphical plot for Elovich equations are presented in Figure 5.5.

It should be noted that the above experiment was conducted with a very high organic loading on the sand in vigorously mixed batch reactors. Therefore, the actual rate for lab column experiments or under field condition is much lower than the rate observed in batch reactors. Factors such as the nature of contamination, type of soil, hydraulic and other environmental and operating conditions will influence the actual rate of solubilization. To accommodate these factors we propose the following relationship which is a modification of equation (5.5)

$$q = 0.178 - 0.0213 \, k \ln(t) \qquad (5.5a)$$

where k is a correction factor whose magnitude will depend on the above conditions and will vary between 0 and 1. Therefore, the reaction rate for residual anthracene on sand can be obtained from equation (5.5a) as

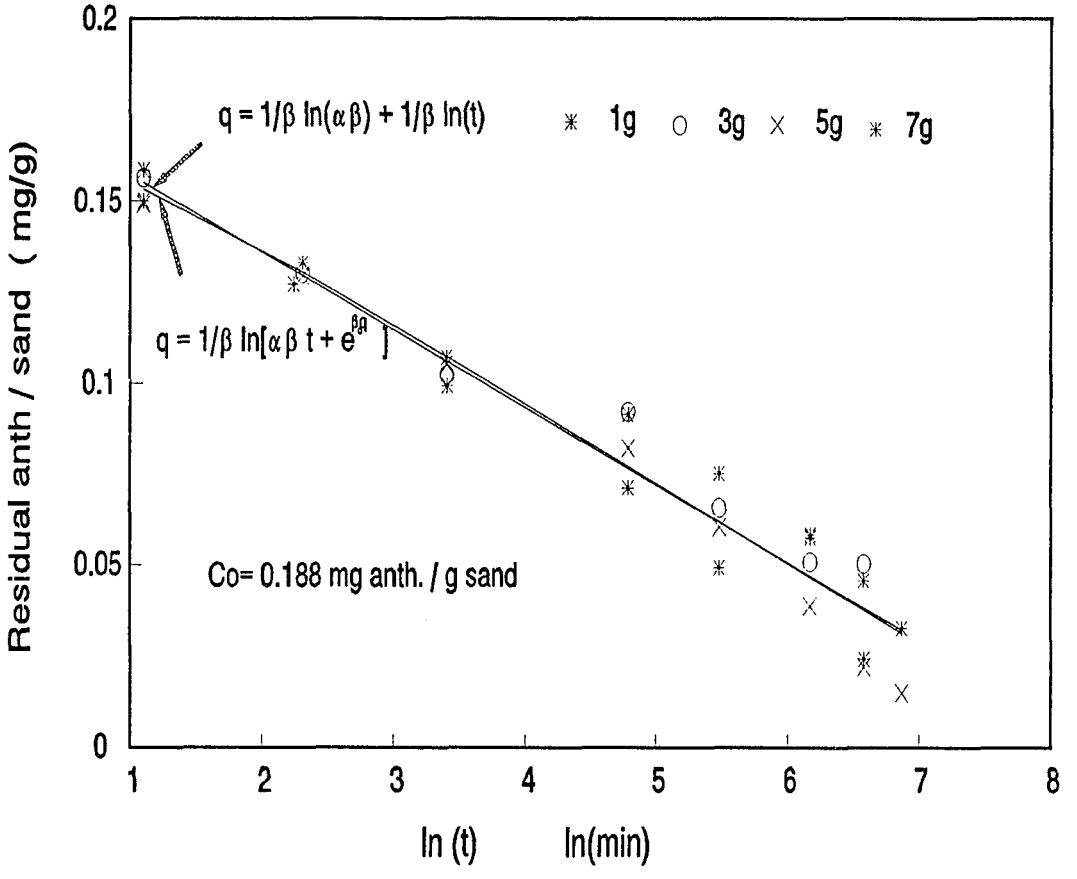

Figure 5.5 Application of Elovich equation to the kinetics of anthracene removal from contaminated sand by 60 mM SDS solution.

$$\frac{dq}{dt} = \frac{-\ 0.0213\ k}{t} \qquad (5.6)$$

Results and Modeling of Column Experiments

The purpose of the first column experiment was to compare the effectiveness of water and 60 mM SDS solution in mobilizing anthracene. The column was filled with sand contaminated with 188 mg anthracene/kg sand. Water or 60 mM SDS solution was pumped. The percentage of anthracene remaining in the sand column as a function of the effluent volume is presented in Figure 5.6. Anthracene remaining in soil was calculated by mass balance from the concentration of anthracene in the effluents. Anthracene concentration in the first pore volume was very low. This observation is consistent with the fact that the solubility of anthracene in water is very low and the first pore volume of surfactant solution displaces the pore spaces of the column filled with water only. After the passage of the first pore volume, the anthracene remaining in the column was observed to decline in a linear fashion. This constant rate of decline is due to the fact that the effluents reached the saturation or limited solubility of anthracene for the surfactant concentration used. After passing 2300 ml of surfactant, the solubilizing medium pumped to the column was switched to water, this resulted in no additional removal of anthracene. This observation confirms the inadequacy of water to solubilize anthracene from sand under dynamic conditions. After passing 1300 ml of water, the solubilizing medium pumped to the column was switched back to 60 mM SDS. After switching, the rate of anthracene removal from the soil column, as noted by the slope of the line, reverted to the

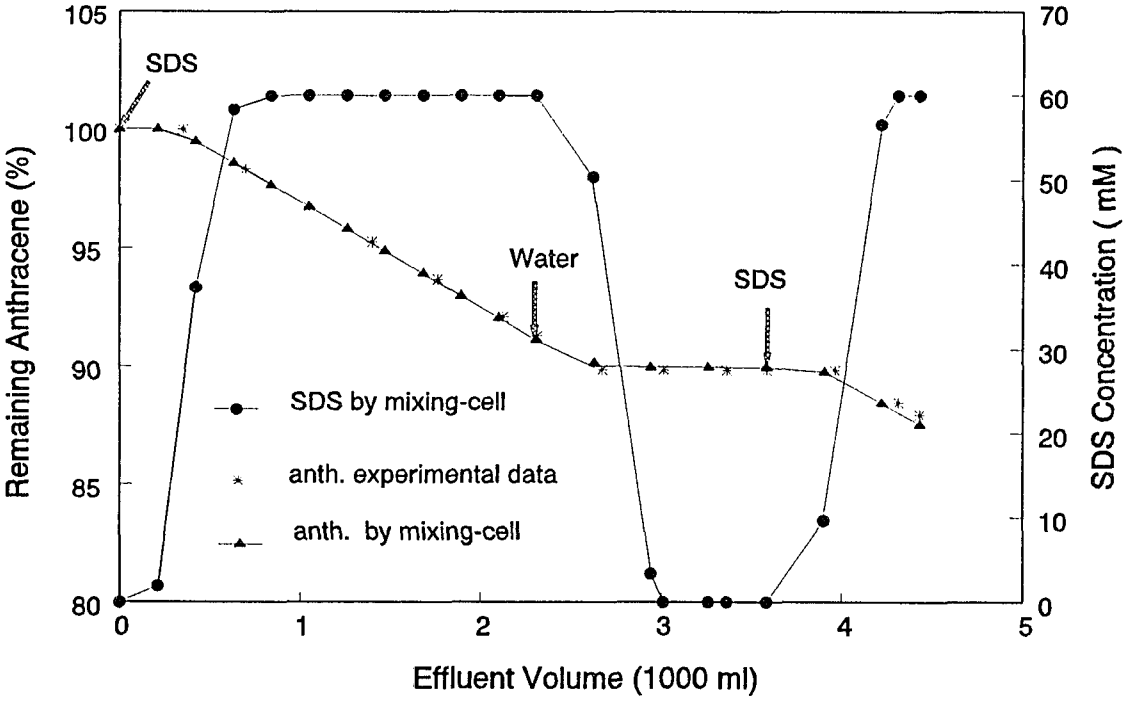

Figure 5.6 Column experiment I (high contamination = 188 mg anth/kg soil): data and the prediction by mixing-cell model.

previous level. Because of the high initial concentration of anthracene in the sand column, anthracene concentration of the effluent still reached the limited solubility. To verify the trend of this experiment for low anthracene concentration (19.2 mg anthracene/ kg sand), another column experiment was performed with 60 mM SDS solution. Anthracene remaining in the column was observed to decrease to less than 10 percent of the original amount after collecting 4100 ml effluent (Figure 5.7).

A numerical method, the mixing cell concept, is applied to simulate the one-dimensional column washing process. The mixing-cell concept has been applied to solute transport of non-reactive or reactive components in soil and groundwater (Dance and Reardon, 1983). The mixing-cell concept treats a column as a number of discrete elements with length Δx, the components of which are thoroughly mixed so that the concentration is homogeneous in each element. Therefore, a mixing-cell concept is simple and easy to simulate the convective-dispersive process in a column.

The convective-dispersive equation with reactions is a general equation describing solute transportation in groundwater. For one dimension it is

$$\frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial x^2} - v \frac{\partial c}{\partial x} + R \qquad (5.7)$$

where c is the concentration of solute in liquid phase (M/L^3); t is time (T); x is distance (L); v is the pore velocity of groundwater (L/T); D is the dispersion coefficient (L^2/T); and R is the reaction rate term ($M/L^3/T$). If initial and boundary conditions are given as $c(x,0)=0$; $c(0,t)=1.0$; and $\partial c/\partial x|_{x\to\infty}=$ finite constant, then equation (5.7) was solved by Carslaw and Jaeger (1959). The solution is

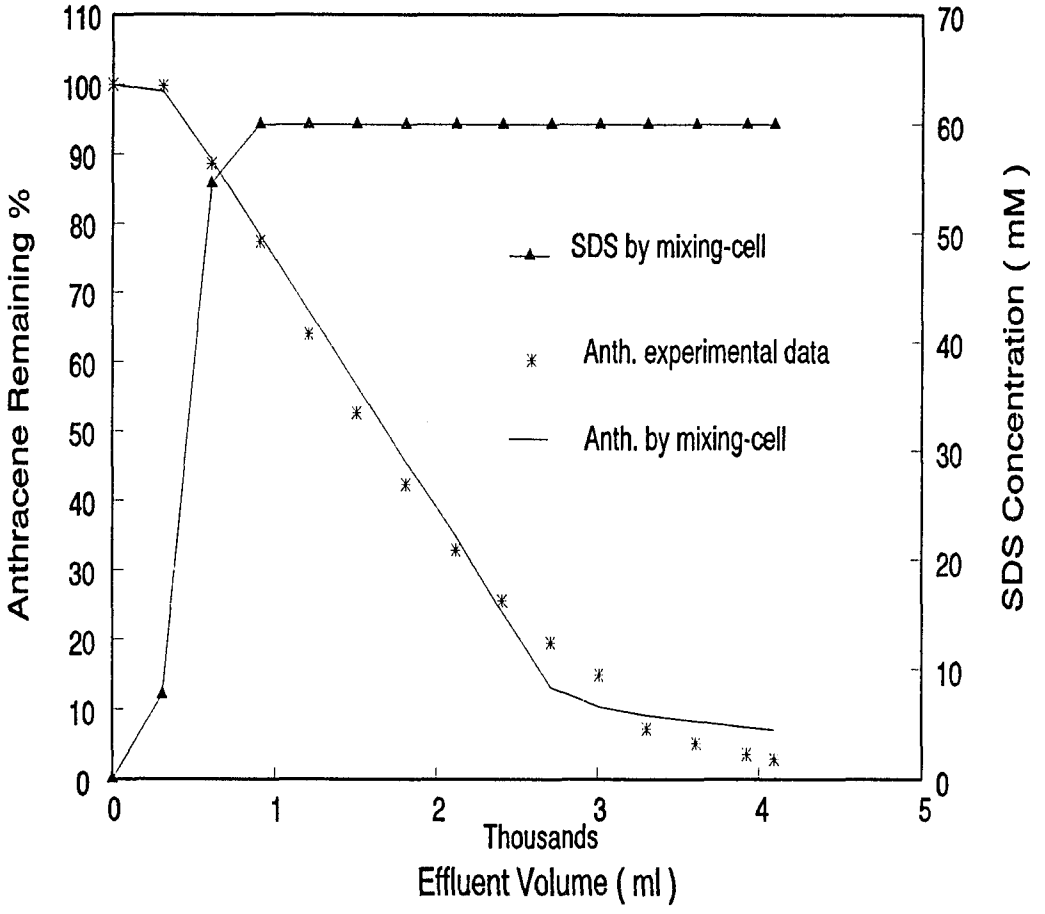

Figure 5.7 Column experiment II (low contamination = 19.2 mg anth/kg soil): data and the prediction by mixing-cell model.

$$c\ (x,\ t) = A\ (x,\ t) + B\ (x,\ t) \tag{5.8}$$

where $$A(x,t) = \frac{1}{2}\ \mathrm{erfc}\left(\frac{x-vt}{2(Dt)^{1/2}}\right) + \frac{1}{2}\ \exp\left(\frac{vx}{D}\right)\ \mathrm{erfc}\left(\frac{x+vt}{2(Dt)^{1/2}}\right)$$

$$B(x,t) = R\ \left[\ t + \frac{x-vt}{2v}\ \mathrm{erfc}\left(\frac{x-vt}{2(Dt)^{1/2}}\right) - \frac{x+vt}{2v}\ \exp\left(\frac{vx}{D}\right)\ \mathrm{erfc}\left(\frac{x+vt}{2(Dt)^{1/2}}\right)\ \right]$$

We can use the mixing-cell concept to solve the same equation. Each element is indicated with an index i and the time axis was composed of a number of discrete time steps with a length Δt, each denoted by an index j. Due to mass balance considerations, the solute concentration c at time $(j+1)\Delta t$ in cell number i is given as follows:

$$c_{i,j+1} = c_{i,j} + \left(\frac{v\ \Delta t}{\Delta x}\right)\ (c_{i-1,j} - c_{i,j}) + R\ \Delta t. \tag{5.9}$$

Mathematically, this mixing-cell concept is equivalent to the backward finite difference method without the dispersive term. Even when a dispersive term is included in the mixing-cell concept, the dispersive term can be eliminated by selecting an optimal time interval, Δt (van Ommen, 1985). The expression of the mixing-cell concept for the general equation is

$$\frac{c_{i,j+1} - c_{i,j}}{\Delta t} = -\ v\ \left(\frac{c_{i,j} - c_{i-1,j}}{\Delta x}\right) + \left(\frac{v^2\ \Delta t}{2} - \frac{v\ \Delta x}{2} + D\right)\ \left(\frac{\partial^2 c}{\partial x^2}\right) + R. \tag{5.10}$$

If

equation (5.10) reduces to

$$\frac{v^2\,\Delta t}{2} - \frac{v\,\Delta x}{2} + D = 0, \tag{5.11}$$

$$\frac{c_{i,j+1} - c_{i,j}}{\Delta t} = -v\,\frac{c_{i,j} - c_{i-1,j}}{\Delta x} + R. \tag{5.12}$$

Equation (5.12) is the same as equation (5.9). Therefore, the finite difference method and mixing-cell concept are similar when

$$\Delta t = \frac{v\,\Delta x - 2D}{v^2}. \tag{5.13}$$

In our column experiments, the anthracene concentration was affected not only by convection and dispersion but also by the kinetics of anthracene solubilization and the limited solubility as we discussed in the batch experiment section. For anthracene, the governing equation is the equation of conservation of mass including hydraulic dispersion and convection:

$$\frac{\partial c}{\partial t} = D\,\frac{\partial^2 c}{\partial x^2} - v\,\frac{\partial c}{\partial x} + f(x, t) \tag{5.14}$$

where c is the concentration of contaminant in the liquid phase (M/L^3); and f(x,t) is an increase of contaminant in liquid phase with time and distance ($M/L^3/T$). Applying the mixing-cell concept, the anthracene concentration on the time $(j+1)\Delta t$ in cell number i is

$$c_{i,j+1} = c_{i,j} + \frac{v\,\Delta t}{\Delta x}(c_{i-1,j} - c_{i,j}) + \rho\,\frac{1-\theta}{\theta}\left(\frac{dq}{dt}\right)\Delta t \tag{5.15}$$

where θ is porosity of the column; and ρ is specific weight of soil (M/L^3). The relation between q and t is shown in the equation (5.6). The initial condition was $c(x,0)=c_0$ and the two boundary conditions were $\partial c/\partial x|_{x=L}=0$ and $c(0,t)=0$. As opposed to solute transportation, solubility of anthracene is limited by the surfactant concentration. The limited solubility of anthracene, c_s, changes with the SDS concentration and the linear function is (Liu and Roy, 1992):

$$C_s(M) = 4.9\times10^{-7} + 0.00119\ (\ C_{surf} - 0.008) \qquad (5.16)$$

where C_{surf} is the concentration of surfactant in liquid phase (M).

Before we calculated the anthracene concentration, we had to know the surfactant distribution in the column. The governing equation for surfactant distribution is,

$$\frac{\partial C_{surf}}{\partial t} = D\ \frac{\partial^2 C_{surf}}{\partial x^2} - v\ \frac{\partial C_{surf}}{\partial x} - F\ (x,\ t) \qquad (5.17)$$

where F(x,t) is the surfactant loss with time and distance ($M/L^3/T$). Since the loss of surfactant on sand can be neglected, i.e., $F(x,t)=0$. After applying the mixing-cell concept, the equation is expressed as

$$C_{surf(i,j+1)} = C_{surf(i,j)} + \frac{v\ \Delta t}{\Delta x}\ (\ C_{surf(i-1,j)} - C_{surf(i,j)}) \qquad (5.18)$$

with initial condition $C_{surf}(x,0)=0$, one boundary condition $\partial C_{surf}(x,t)/\partial x|_{x=L}=0$ and the other boundary condition $C_{surf}(0,t)=Co_{surf}$, where Co_{surf} is the surfactant concentration of inflow.

To model these column experiments, the columns were divided into six elements and the time steps were five minutes. The detailed calculation steps are listed below:

1) apply initial and boundary conditions of surfactant;

2) calculate the distribution of surfactant concentration in each element at time any $j\Delta t$ by equation (5.18);

3) calculate the solubility limit of anthracene in each element at any time $j\Delta t$ by equation (5.16);

4) apply initial condition and boundary conditions of anthracene concentration; and

5) calculate anthracene concentration in each element (equation 5.15) using a time step according to equation (5.13). If $c(i,j) > c_s(i,j)$, $c(i,j) = c_s(i,j)$ and reaction time was not accumulated.

The operating parameters and other experimental conditions for the laboratory scale column experiments which are used in modeling work are listed in Table 5.1. It should be noted that for column one the experiment flow rate was changed after 2300 ml of effluent was collected.

Predictions by the mixing-cell concept model for the two column experiments are also shown in Figure 5.6 and 5.7 with lines. For the first column experiment, anthracene prediction from mixing-cell concept is very close to the experimental data (Figure 5.6). Because of the high organic loading, the constant k for this experiment is equal to 1. For the second column run with low anthracene loading (19.2 mg/kg sand), k was obtained by trial and error. To further evaluate the performance of the

Table 5.1 Column experimental conditions and the parameters in modeling.

Parameters	Column One	Column Two
Pore Velocity (cm/min)	0.364 0.558	0.526
Δx (cm)	5	5
Δt (min)	5	5
D (cm^2/min) (equation 5.13)	0.579 0.926	0.631
k	1.00	0.04
initial contamination mg anth/kg sand	188	19.2

mixing-cell concept, the goodness of fit is checked by calculating the relative squared error (RSE)

$$RSE = \frac{\sum_{t=1}^{m} [\, c(t) - c_c(t) \,]^2}{\sum_{t=1}^{m} [\, c(t) \,]^2} \qquad (5.19)$$

where c(t) is the observed experimental data; and $c_c(t)$ is the predicted points. RSE represents the overall accuracy. If the RSE = 0.0, the prediction will coincide with the experimental data. For the first column, the RSE is 0.03%. For the second column a k value of 0.04 produced the minimum RSE of 0.4%. The calculated SDS concentrations are also shown in the graphs. The anthracene removal is related to the SDS concentration when anthracene is in high loading. For the first column (188 mg/kg sand), the change of anthracene removal is associated with the change of SDS concentration. High removal corresponded to a high SDS concentration. But for the low contamination column, the initial anthracene removal corresponded to the SDS concentration change. Later although SDS is still in high concentration, the removal slowed down because the anthracene concentration in sand was very low at these points. Once again, these phenomena confirm that anthracene cannot be effectively removed from soil by water and the removal is related to the nature of contamination.

The physical meaning of the mixing-cell concept is very clear and it is easy for engineers to understand and apply. It is especially convenient to use the mixing-cell

concept to simulate processes which involve complex boundary conditions and limited conditions such as those encountered in the soil washing process.

Conclusions

Based on the results and discussion of this research, the following specific conclusions can be drawn:

- SDS loss and adsorption of anthracene on sand are negligible.
- Solubilization is the main mechanism for removal of anthracene from contaminated sand and the limited solubility of anthracene in SDS affects the removal.
- The kinetics of anthracene solubilization from contaminated sand into surfactant solution can be expressed using the exponential Elovich equation.
- SDS, an anionic surfactant, can be used successfully for solubilizing hydrophobic organic compounds from sand columns.
- The mixing-cell concept is a reliable and simple numerical method to simulate the sand washing process.

CHAPTER 6
REACTIONS AND TRANSPORT MODELING OF SURFACTANT AND ANTHRACENE IN SOIL WASHING PROCESS

Introduction

The conventional pump-and-treat technology is one of the most widely used techniques for decontamination of the subsurface with non-volatile organics. However, at many sites pump-and-treat technology will require decades of costly operation to achieve the desired levels of cleanup (Haley et al., 1991; Palmer and Fish, 1992). Surfactant soil washing is a promising alternative to promote the solubilization and mobilization of hydrophobic organic contaminants resulting in enhancement of the conventional pump-and-treat method. Several investigations in the last few years have assessed the potential of surfactants to clean the contaminated soils (Ellis et al., 1985; Nash, 1987; Gannon et al., 1989; Abdul and Gibson, 1991; Abriola et al., 1993). Surfactant solutions can greatly enhance the solubility of hydrophobic organic compounds (Gannon et al., 1989; Edwards et al., 1991; Kile and Chiou, 1989). The mobilization is enhanced by reducing the surface tension between soil and entrapped hydrophobic organics (Ang and Abdul, 1991; Fountain et al., 1991). To date, much of the environmental research on surfactant has been concerned with the efficiency of surfactant solubilization and little has been done to predict the behavior and ultimate fate of these compounds in aquifer environments (West and Harwell, 1993).

The purpose of this paper is to develop a mathematical formulation of the surfactant soil washing process which can predict the fate and transport of surfactants

and hydrophobic organics through porous media. Anthracene was selected as the model hydrophobic organic compound because it is nearly insoluble in water (0.073 mg/l) and it has been recommended as a target contaminant by Superfund Standard Analytical Reference Matrix (Esposito et al., 1988). Sodium Dodecylsulfate (SDS), one of the well investigated surfactant (Rosen, 1989; Vold and Vold, 1983), was chosen as the representative surfactant because it is biodegradable (Swisher, 1987; Shiau et al. 1992) and can greatly increase the solubility of anthracene. The solubility of anthracene is a linear function of SDS concentration above the critical micelle concentration (CMC) of SDS (Liu and Roy, 1992). The mathematical model to be developed is based on an equilibrium isotherm for SDS and a non-equilibrium rate-limited expression for anthracene. One-dimensional column experiments were designed to obtain the information necessary to calibrate and verify the model for the fate and transport of surfactant and anthracene through soil matrices.

Materials and Methods

Chemicals

High purity (99.5%) reagent grade Sodium Dodecylsulfate (SDS) was obtained from Life Technologies, Inc. (Gaithersburg, MD). The chemical formula of SDS is CH_3-$(CH_2)_{11}$-$SO_4^-Na^+$ and its molecular weight is 288.38. The critical micelle concentration (CMC) of SDS is 8.0 mM. Sodium Chloride was obtained from EM Science (Gibbstown, NJ). Anthracene ($C_{14}H_{10}$) (99%), was purchased from Sigma Chemical Co. (St. Louis, MO). Anthracene's molecular weight is 178.24 and boiling

point is 342°C. The solubility of anthracene in water is 0.073 mg/l (Dzombak and Luthy, 1983).

Materials

A sample of fine sand was obtained from Industrial Sand Co. (Baton Rouge, LA). Sieve analysis was performed on the sand sample and showed that the d_{10} = 0.11 mm and the uniformity coefficient (d_{60}/d_{10}) was 1.76. Since the uniformity coefficient was less than 2.0, the sand sample was classified as a uniform fine sand. A soil sample was obtained from the subsoil of a lot adjacent to the Louisiana State University greenhouse near Student Recreation Center. The soil sample was air dried, and pulverized particles larger than 2 mm were discarded. Organic content, pH and exchangeable ions of the soil and sand were measured by the Louisiana State University Agriculture Center using standard techniques. Texture was measured by hydrometer method. The properties of the soil and sand are shown in Table 6.1. According to the classification of texture triangles (Loveland, 1991), the soil used is a silty clay loam. It has low organic content but contains a high content of divalent cations. Mineral analysis shows that the soil sample contains a small quantity of Montmorillonite.

Measurements

SDS was measured according to the Standard Methods for the Examination of Water and Wastewater (APHA/AWWA/WPCF, 1990). Chloride ion concentration was measured by using a specific ion electrode and a reference electrode from Microelectrodes. Inc. (Londonderry, NH). Anthracene analysis was performed using

Table 6.1 The laboratory testing results of soil and sand.

ITEMS	SOIL	SAND
Texture sand % silt % clay %	 21 49 30	 >99 < 1
pH	4.8	8
organic content %	0.47	≈0
CEC meq/kg	8.96	0.4
Exchangeable Ions (meq/100g) K Na Ca Mg	 2.61 0.83 96.66 12.18	 0.13 0.13 3.49 0.66
Minerals	Illite Kaolinite Montmorillonite quartz	quartz feldspar

a HPLC (Series 1050, Hewlett Packard, Avondale, PA). For the HPLC, a pre-packed column, Envirosep-pp 125×3.2 (Phenomenex Co., Torrance, CA) was used, and the general method provided by the column manufacturer was used. All soil samples for analysis of anthracene were centrifuged for 7 minutes at 14,000 rpm (Model 5415, Brinkmann Instruments Inc., Westburg, NY) and were then further filtered through a 0.45 μm teflon syringe filter (Nalge Co., Rochester, NY).

Anthracene Batch Experiment

Anthracene adsorption experiments were conducted at two concentrations of SDS solution, 30 mM and 60 mM. First a SDS solution with extra quantity of anthracene crystals was stirred for 48 hours to reach the limited solubility of anthracene. Then the solution was allowed to stand over night to insure that the solution was not over saturated. It was then filtered through a 0.45 μm membrane to remove the extra anthracene solid. The filtrate was diluted into a series of different anthracene concentrations using the same SDS solution. Soil was added to these solutions and this suspension was shaken in orbital incubator at 25°C (Sanyo Gallenkamp Plc., Bensenville, IL). The weight ratio of liquid to soil was 10 to 1 and the containers were 250 ml polycarbonate centrifuge bottles (International Equipment Company, Needham Hights, MA). The samples were taken at 2, 8, 22 hours and then every 22 hours for analysis. After 88 hours of shaking the bottles were centrifuged at 10000 rpm for 15 min (B22 centrifuge, 875 rotor, International Equipment Company, Needham Hights, MA), the supernatant was collected and analyzed. For each concentration, the samples were taken from duplicated or

triplicated runs, and a blank was used as a control to account for the adsorption of anthracene on the wall of the bottles. After adsorption test, pure SDS solution was added into the bottles which contained contaminated soil and the mixture were shaken in the incubator. Samples were taken along with the reaction time and anthracene concentration in aqueous phase was measured for desorption test.

SDS Batch Experiment

10 grams of air-dried soil was placed in glass bottles containing 50 ml of a range of concentrations of SDS solution. The mixture were shaken in a rotary shaker for 24 hours. Oberoi et al. (1986) reported that 80 % equilibrium between SDS and montmorillonite was established within 2.5 hours. The average biodegradation time of SDS in surface environment is about 10 to 30 days (Swisher, 1987). The 24 hours contact time used in this study is considered to be sufficient for the equilibrium condition and to avoid the biodegradation problem. The supernatant was collected, centrifuged (Brinkmann Centrifuge Model 5415) at 14,000 rpm for 10 minutes, and then analyzed. Samples were taken from duplicated or triplicated runs, and a blank was used as a control to account for the adsorption of the chemical on the glass surface. The surfactant concentration in the liquid phase was monitored and the non-aqueous phase surfactant was determined by the difference between the original and the final aqueous concentration of surfactant.

Column Experiments

150 or 250 grams of soil was placed without packing into 3 or 5 cm long glass column respectively with a 6.35 cm ID. At the effluent end, there was a stone filter

which was used to prevent soil washout. The column was saturated with DI water for 2 to 3 hours to drive out the entrapped air. Samples were collected every 30 or 60 minutes by a fraction collector.

Two experiments were performed for the tracer, Cl^-. One used a 5 cm long column with a pumping velocity of 4.10×10^{-3} cm/min and the other utilized a 3 cm long column with the velocity changing from 3.63×10^{-3} to 3.11×10^{-3} cm/min after the Cl^- pulse. The procedures were the same for both columns. First, pure surfactant solution (30 mM) was pumped into the columns to displace the DI water; then the pumping solution was switched to 30 mM surfactant solution containing 30 mM Cl^-. After pumping in about one pore volume of Cl^- solution, the pumping solution was switched back to the pure surfactant solution.

Two experiments were performed for SDS and anthracene transport. The first experiment was performed using 30 mM SDS solution with an inflow anthracene concentration of C_o= 2.98 mg/l and the second column experiment was performed using 60 mM SDS solution with an inflow anthracene concentration of C_o= 7.87 mg/l. First, pure surfactant solution was pumped into the columns to displace DI water. After pumping approximately 1 pore volume of pure SDS solution, the pumping solution was switched to the same concentration of SDS solution but with the anthracene concentration C_o. When the change of anthracene concentration in the effluent became small, the pumping solution was switched back to pure SDS solution.

Experimental Results and Modeling

Dispersive Coefficient

Chloride ions are used as the tracer to determine the dispersive coefficient for the soil matrix by using curve fitting technique to the experimental data. Mass conservative model for a tracer can be expressed using the one-dimensional convective-dispersive solute transport equation without any reaction terms:

$$\frac{\partial c}{\partial t} = D_x \frac{\partial^2 c}{\partial x^2} - v \frac{\partial c}{\partial x} \qquad (6.1)$$

where c is the aqueous solute concentration in the solution (M/L^3); t is time (T); D_x is dispersive coefficient (L^2/T); v is the pore velocity (L/T); and x is the coordinate (L). Analytical solutions of equation (6.1) for different initial and boundary conditions have been reported by van Genuchten and Alves (1982). Equation (6.1) with the following initial and boundary conditions is applied to obtain D_x by fitting technique to the experimental Cl^- results:

initial condition: $c(x,t) = c_i, \quad t < t_o$ (6.1a)

and boundary conditions 1). $c(0,t) = c_o, \quad t_o \le t \le t_c$

$0, \quad t > t_c$ (6.1b)

2). $\frac{\partial c}{\partial x} = 0 \quad x = L \; ; \; t = t.$ (6.1c)

where t_o is the time at which Cl^- is introduced into the column; and t_c is the time at the end of the Cl^- pulse. The analytical solution and approximate solution of equation

(6.1) with the above initial and boundary conditions are given by Cleary and Adrian (1973). The approximate solution is

$$A(x,t) = \frac{1}{2}\,\mathrm{erfc}\left[\frac{x-vt}{2(D_x\,t)^{0.5}}\right] + \frac{1}{2}\exp\left(\frac{vx}{D_x}\right)\mathrm{erfc}\left[\frac{x+vt}{2(D_x\,t)^{0.5}}\right]$$
$$+ \frac{1}{2}\left[2+\frac{v\,(2L-x)}{D_x}+\frac{v^2\,t}{D_x}\right]\exp(vL/D_x)\,\mathrm{erfc}\left[\frac{(2L-x)+vt}{2(D_x\,t)^{0.5}}\right] \qquad (6.1d)$$
$$-\left(\frac{v^2\,t}{\pi\,D_x}\right)^{0.5}\exp\left[\frac{vL}{D_x} - \frac{R}{4\,D_x\,t}(2L-x+v\,t)^2\right].$$

When applying the approximate solution to the 3 cm column experiment, two sets of initial condition and boundary conditions were used because of the velocity change. The results are presented in Figure 6.1 and Figure 6.2. The concentration of Cl^- is expressed as a relative concentration (C/C_o) and the volume of the effluent is obtained by multiplying the flow rate by time. The plot of three pairs of pore velocities and dispersive coefficients is presented in Figure 6.3. It shows that the dispersive coefficient is a linear function of velocity ($R^2 = 0.99$).

Equilibrium Isotherm for SDS

When SDS is passed through soil columns, reactions such as adsorption, ion exchange, precipitation will occur (Walker et al., 1978). Batch experiments were conducted to establish the equilibrium condition of SDS and the native soil. Non-aqueous phase surfactant concentrations versus aqueous phase surfactant concentrations for this experiment are shown in Figure 6.4. Because of the trend noted for experimental results (Figure 6.4), the results of SDS loss on soil have been divided into three regions: below CMC, above CMC and greatly above CMC. The CMC of

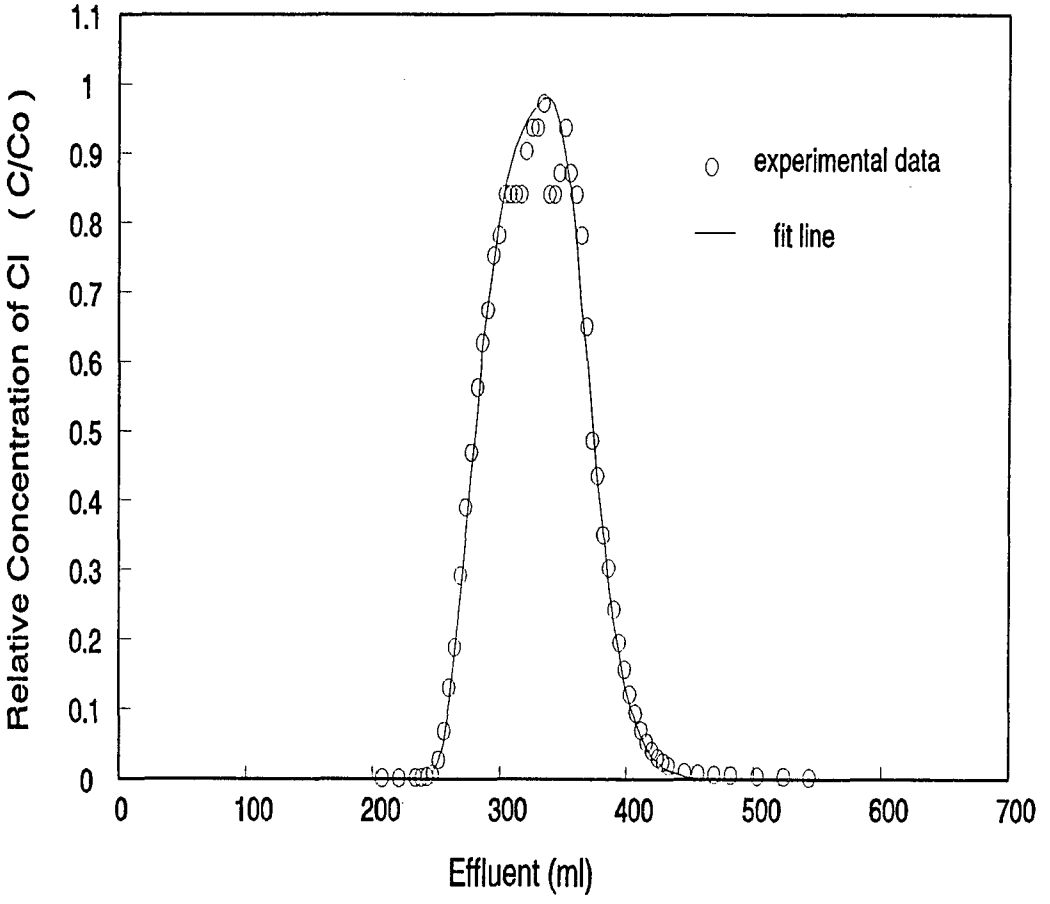

Figure 6.1 Tracer experiment I: 5 cm long glass column, v = 4.1E-3 cm/min and D_x = 0.00157 cm^2/min.

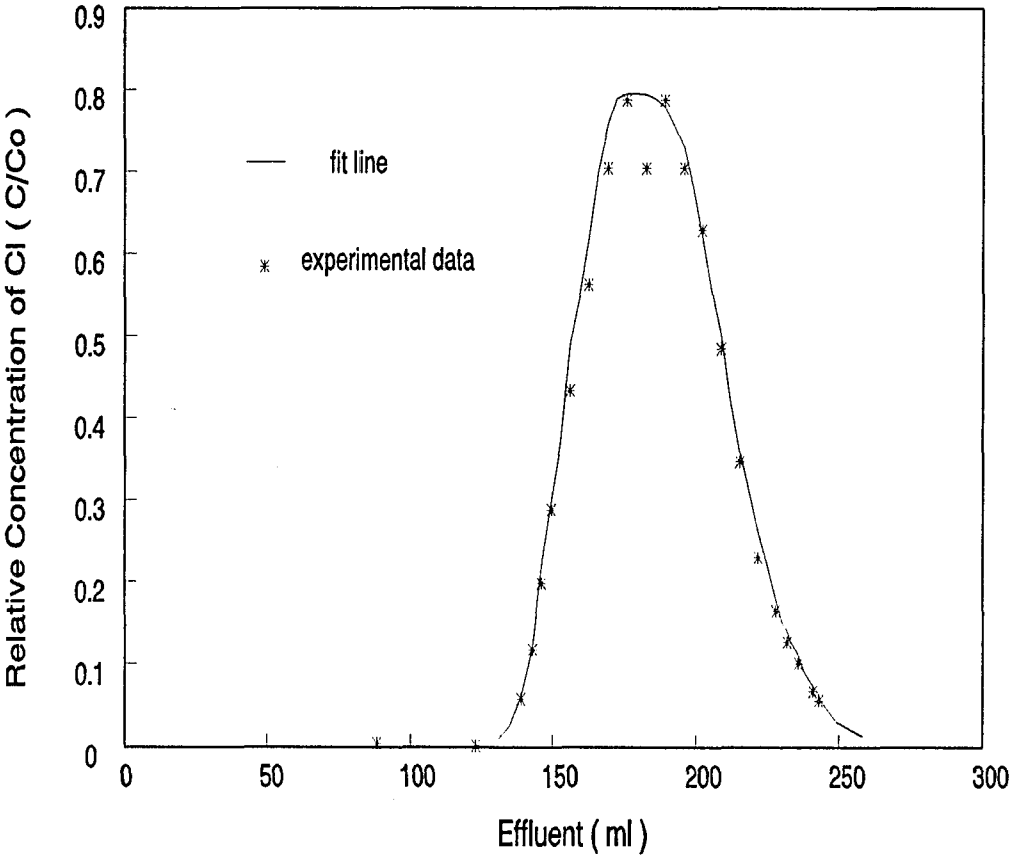

Figure 6.2 Tracer experiment II: 3 cm long glass column, v = 3.6E-3 cm/min, D = 0.00152 cm^2/min; v = 3.1E-3 cm/min, D_x = 0.00148 cm^2/min.

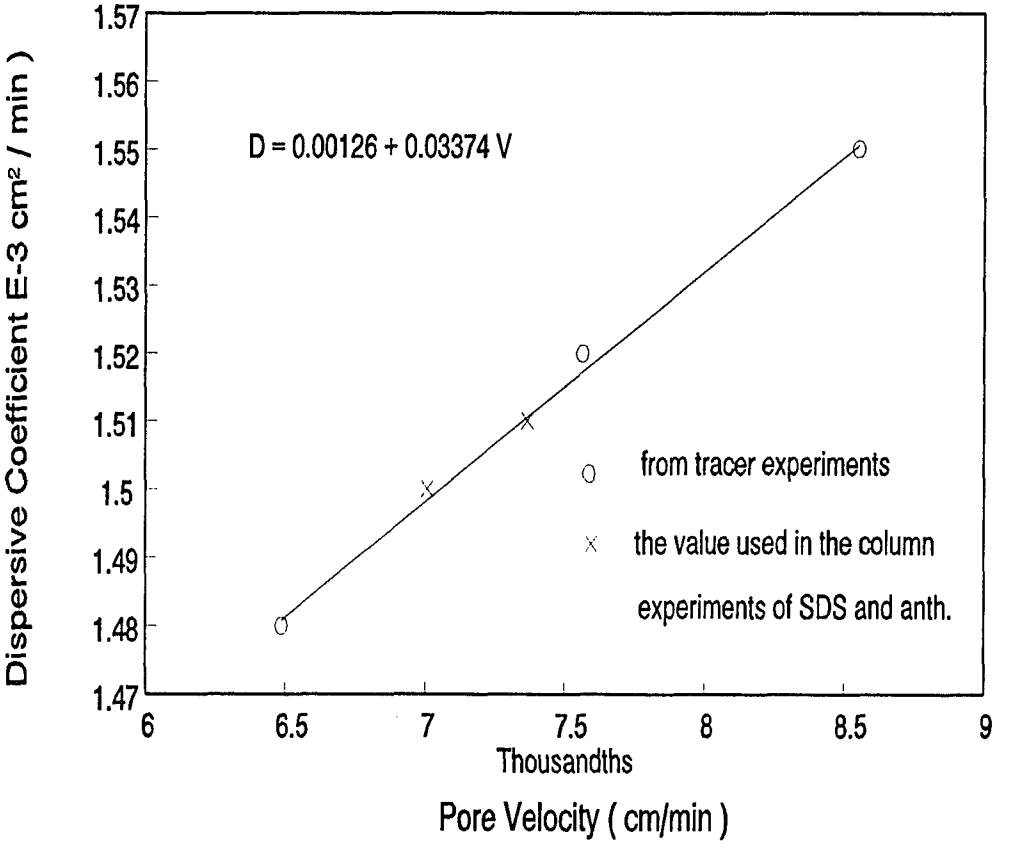

Figure 6.3 The relation of pore velocity and dispersive coefficient.

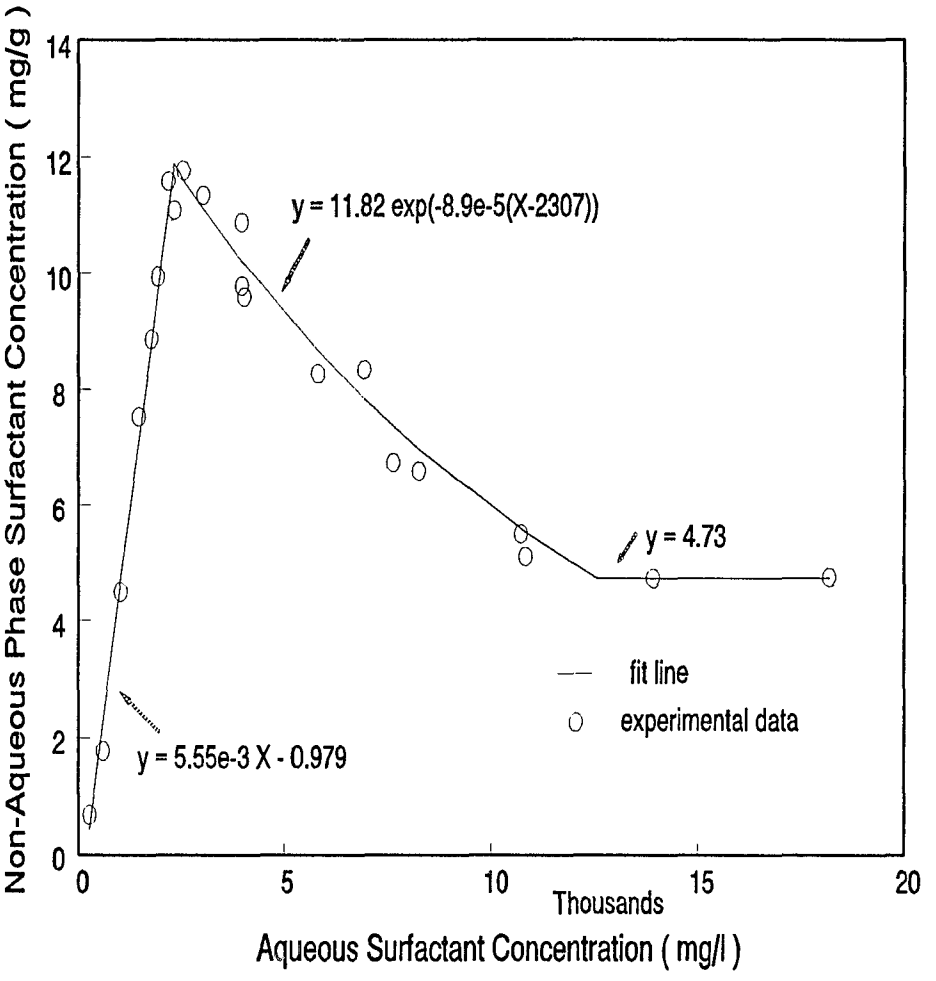

Figure 6.4 The mathematical models and the relationship between SDS loss on soil and aqueous equilibrium concentration.

SDS is a critical point of difference. Using curve fitting techniques to the data presented in Figure 6.4, the mathematical expressions of the three regions are:

$$S_{surf} = \begin{cases} 5.55E\text{-}3C_{surf} - 0.979 & C_{surf} < CMC = 2307 \text{ mg/l} \\ 11.821\exp[-8.9E\text{-}5(C_{surf}-2307)] & CMC \le C_{surf} \le 12580 \text{ mg/l} \\ 4.73 \text{ mg surf/g soil} & C_{surf} > 12580 \text{ mg/l} \end{cases} \quad (6.2)$$

where S_{surf} is the concentration of surfactant in non-aqueous phase (mg surf/ g soil); and C_{surf} is the concentration of surfactant in aqueous phase (mg/l).

Quasi-equilibrium Isotherm for Anthracene

Unlike SDS, the time required to reach equilibrium level of anthracene for adsorption experiment appears to be much longer. Furthermore, the presence of surfactants increases the solubility of anthracene in aqueous phase. The change of anthracene concentration with time in 60 mM SDS solution is presented in Figure 6.5. The adsorption rate of anthracene in 30 mM SDS solution showed the same trend (Figure 6.6). The change of aqueous phase anthracene concentration in batch adsorption experiment was observed to be rapid during the first 8 hours followed by a slow rate of change reaching a plateau at approximately 88 hours, which is considered to be the quasi-equilibrium time for anthracene in SDS solution with soil. The results of quasi-equilibrium shown in Figure 6.7 were noted to follow Langmuir type isotherms:

$$\text{for} \quad 30 \text{ mM SDS solution}, \qquad S = \frac{A\,C}{b + C} = \frac{16.97\,C}{1.32 + C} \qquad (6.3)$$

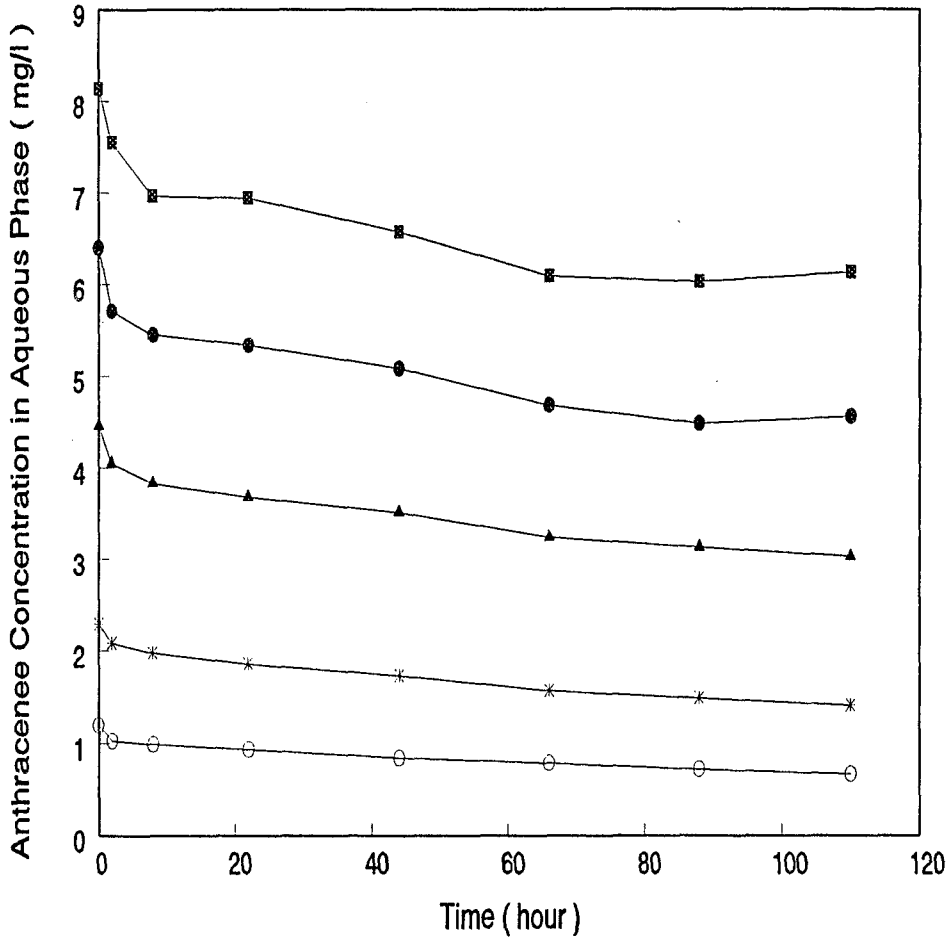

Figure 6.5 The change of aqueous anthracene concentration in SDS (60 mM) solution for different initial anthracene concentrations (■ Co=8.14; ● Co=6.40; ▲ Co=4.46; * Co=2.29; ○ Co=1.19 mg/l).

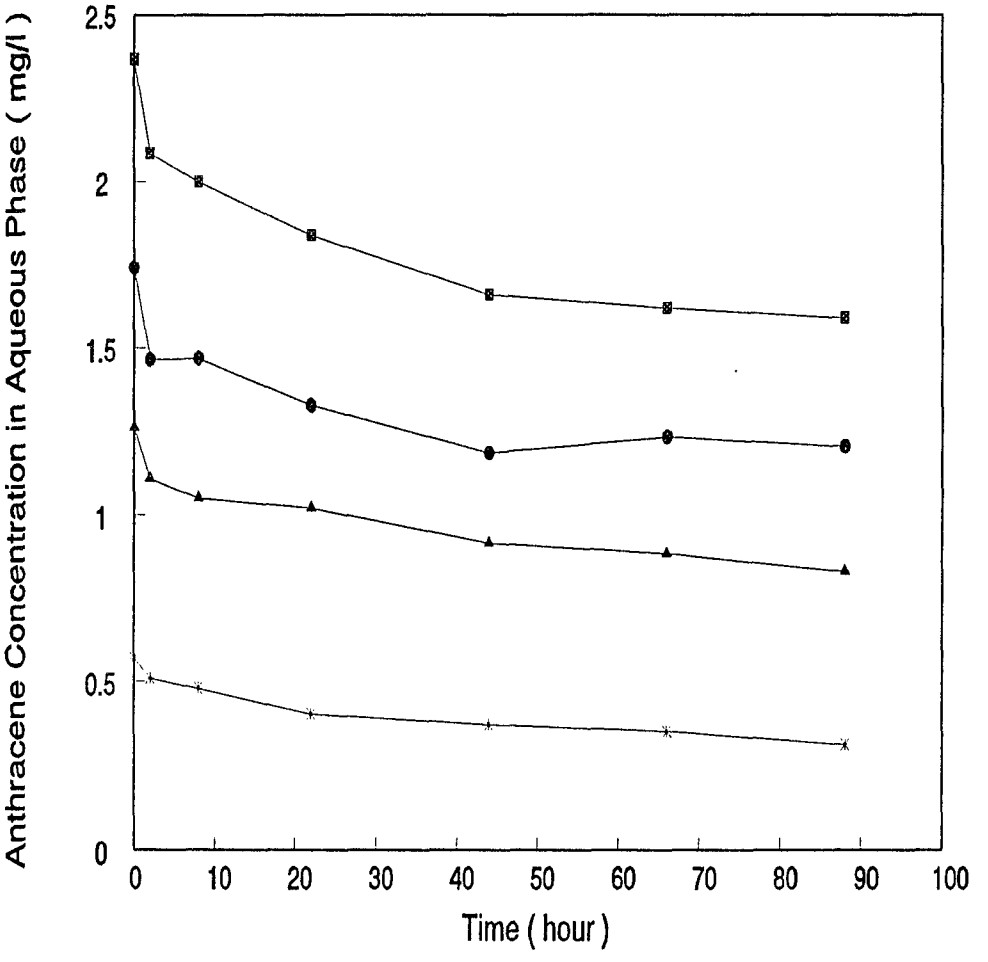

Figure 6.6 The change of aqueous anthracene concentration in SDS (30 mM) solution for different initial anthracene concentrations (■ Co=2.37; ● Co=1.74; ▲ Co=1.26; * Co=0.567 mg/l).

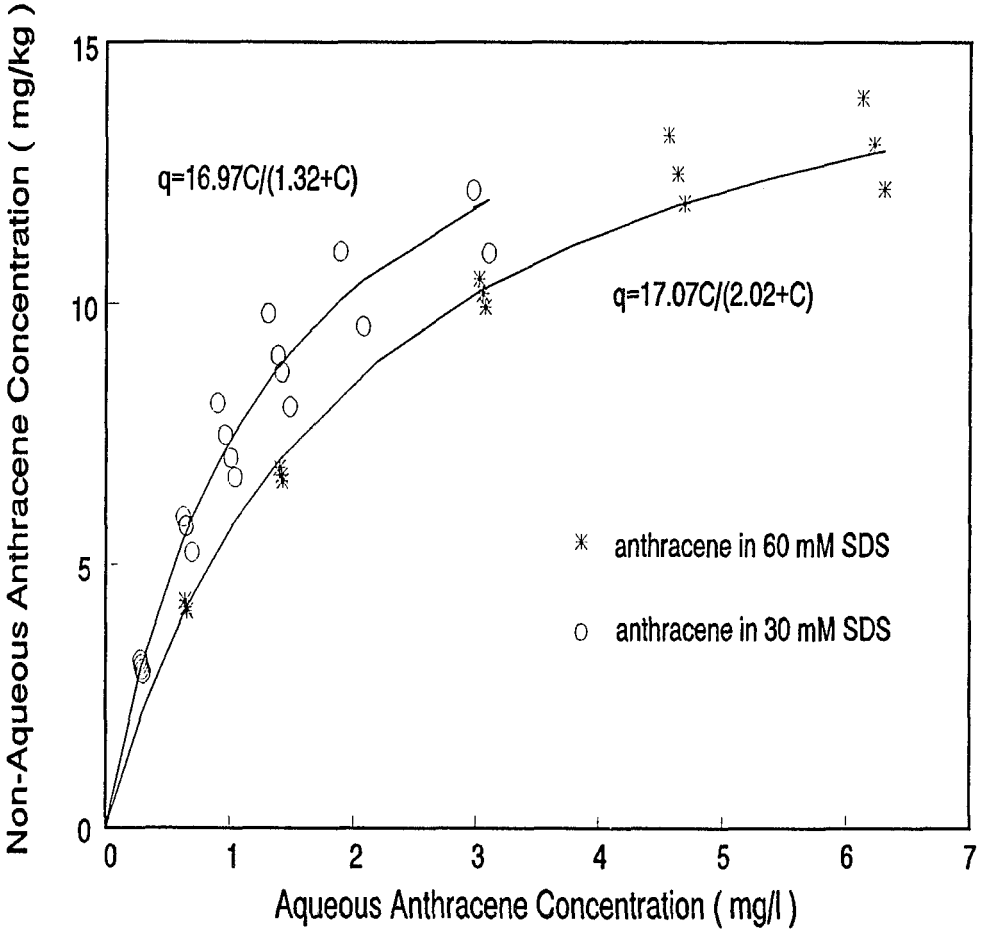

Figure 6.7 Anthracene quasi-equilibrium isotherm on native soil in the presence of SDS (88 hours).

$$\text{for} \quad 60 \text{ mM SDS solution}, \qquad S = \frac{A\,C}{b + C} = \frac{17.07\,C}{2.02 + C} \qquad (6.4)$$

where C is the concentration of anthracene in aqueous phase (mg/l); S is the concentration of anthracene in non-aqueous phase (mg/kg soil); A is the ultimate adsorption capacity (mg/kg); and b is the energy constant (mg/l). The R^2 of 1/S versus 1/C are 0.98 and 0.99 for 30 and 60 mM solution, respectively (Figure 6.8). Statistical analysis is applied to check the values of the slope and intercept of the two lines in Figure 6.8. The hypotheses test shows that the values of the intercept are same but the values of the slope are different for these two lines. That means the values of ultimate adsorption capacity (A) are same and the values of energy constant (b) are different for anthracene adsorption in 30 or 60 mM SDS solution.

After the completion of adsorption, desorption experiments were performed using the soil sample loaded with anthracene. The initial anthracene concentration in liquid phase was calculated based on the amount of anthracene which was left in the liquid phase after the adsorption experiment. The results of anthracene desorption in 60 mM SDS solution are shown in Figure 6.9. During the early stages of the experiments, the anthracene concentration in the aqueous phase was observed to increase followed by a decreasing trend with time. Anthracene desorption using 30 mM SDS solution showed the same trend (Figure 6.10). From the results of desorption experiments it appears that the anthracene adsorption isotherm is non-singular with this soil. It should be noted that in the case of singular isotherm the

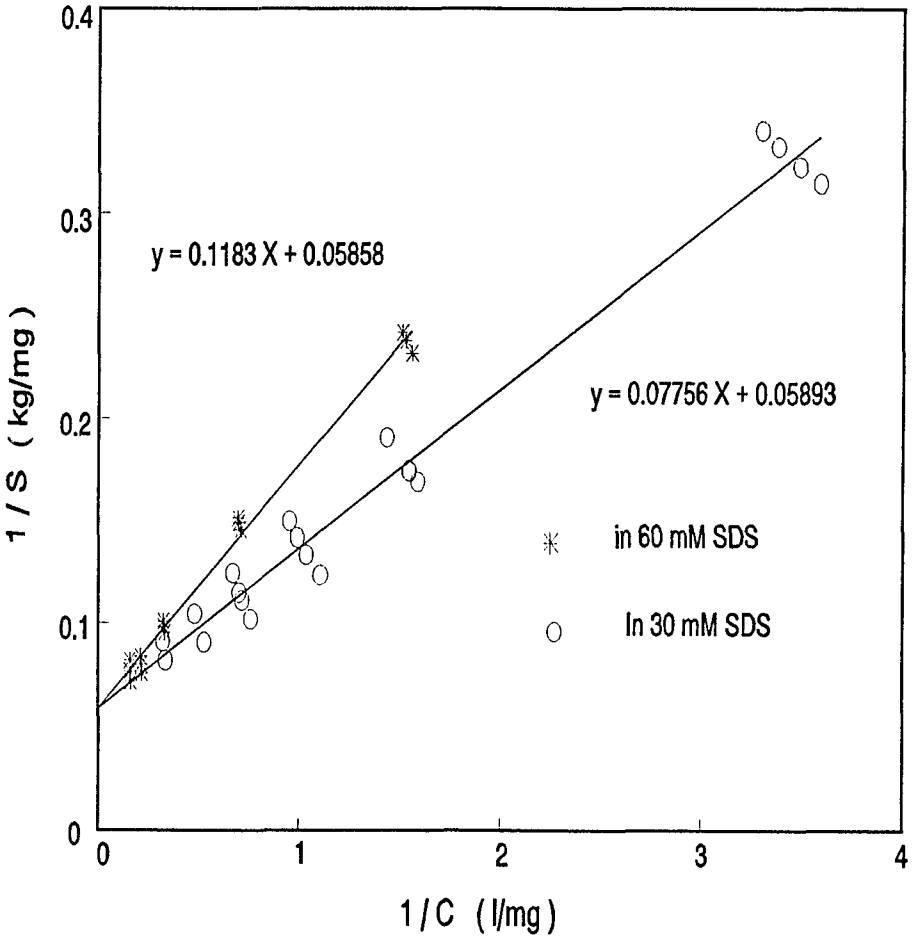

Figure 6.8 The linear form of Langmuir isotherm (R^2= 0.98 for anthracene in 30 mM SDS and R^2= 0.99 for anthracene in 60 mM SDS with soil).

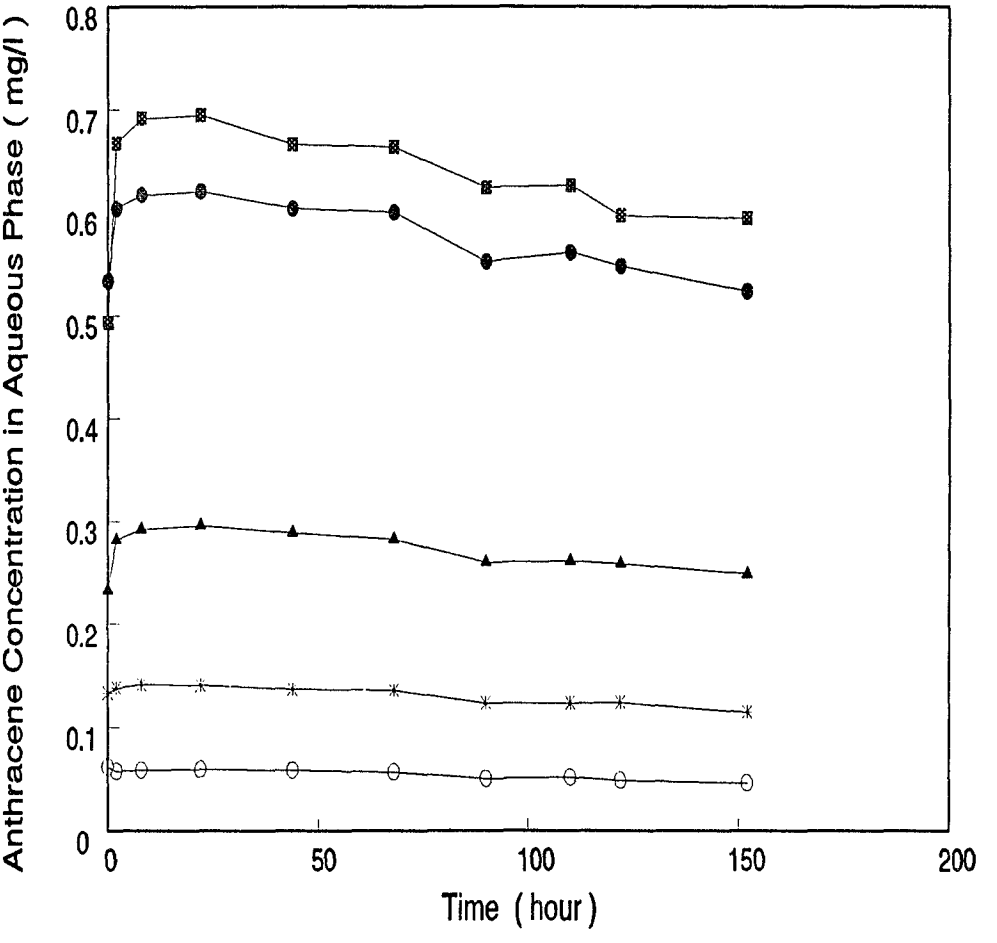

Figure 6.9 Desorption rate of anthracene in the presence of SDS (60 mM) with different initial anthracene concentrations (■ Co=0.493; ● Co=0.533; ▲ Co=0.233; * Co=0.133; ○ Co=0.062 mg/l).

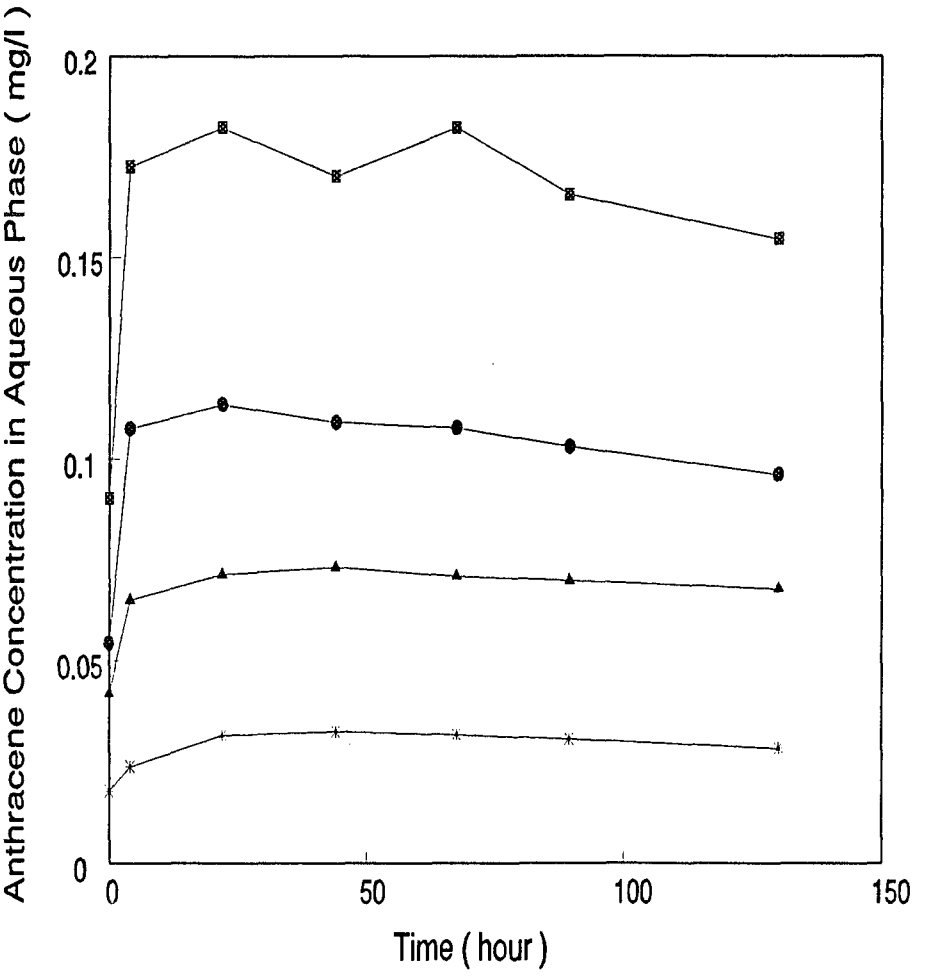

Figure 6.10 Desorption rate of anthracene in the presence of SDS (30 mM) with different initial anthracene concentrations (■ Co=0.090; ● Co=0.0543; ▲ Co=0.0417; * Co=0.0178 mg/l).

aqueous phase concentration of solutes corresponding to adsorbed phase solutes concentration is same for both adsorption and desorption. Therefore, the chosen 88 hours is not a real equilibrium time for adsorption/desorption of anthracene on soil and designating the adsorption isotherm as the quasi-equilibrium isotherm seems to be appropriate.

Column Experiments and Governing Equations

In order to study the process of dissolution and transport of anthracene in SDS solution, two column experiments were conducted. The procedure are similar for both experiments. After about 1 or 1.5 pore volume of pure surfactant solution was pumped into the column, the pumping solution was switched to the same concentration of SDS solution but with the anthracene concentration C_o. When the change of anthracene concentration in the effluent became small, the pumping solution was switched back to pure SDS solution. The experimental data and break-through curves of anthracene and SDS are shown in Figure 6.11 (30 mM SDS and anthracene C_o= 2.98 mg/l) and Figure 6.12 (60 mM SDS and anthracene C_o= 7.87 mg/l).

When the solutes react with the matrix material, a reaction term is added to one-dimensional mass conservative equation (6.1). Equation (6.1) now becomes

$$\frac{\partial C}{\partial t} + \frac{\rho\,(1-\theta)}{3\,\theta}\,\frac{\partial S}{\partial t} = D_x\,\frac{\partial^2 C}{\partial x^2} - v\,\frac{\partial C}{\partial x} \qquad (6.5)$$

where S is the non-aqueous solute concentration (M/M); ρ is the specific weight of the soil (M/L^3) and θ is the porosity of the matrix. Previous experiment showed that in comparison with the native soil, the fine sand had little adsorption affinity for

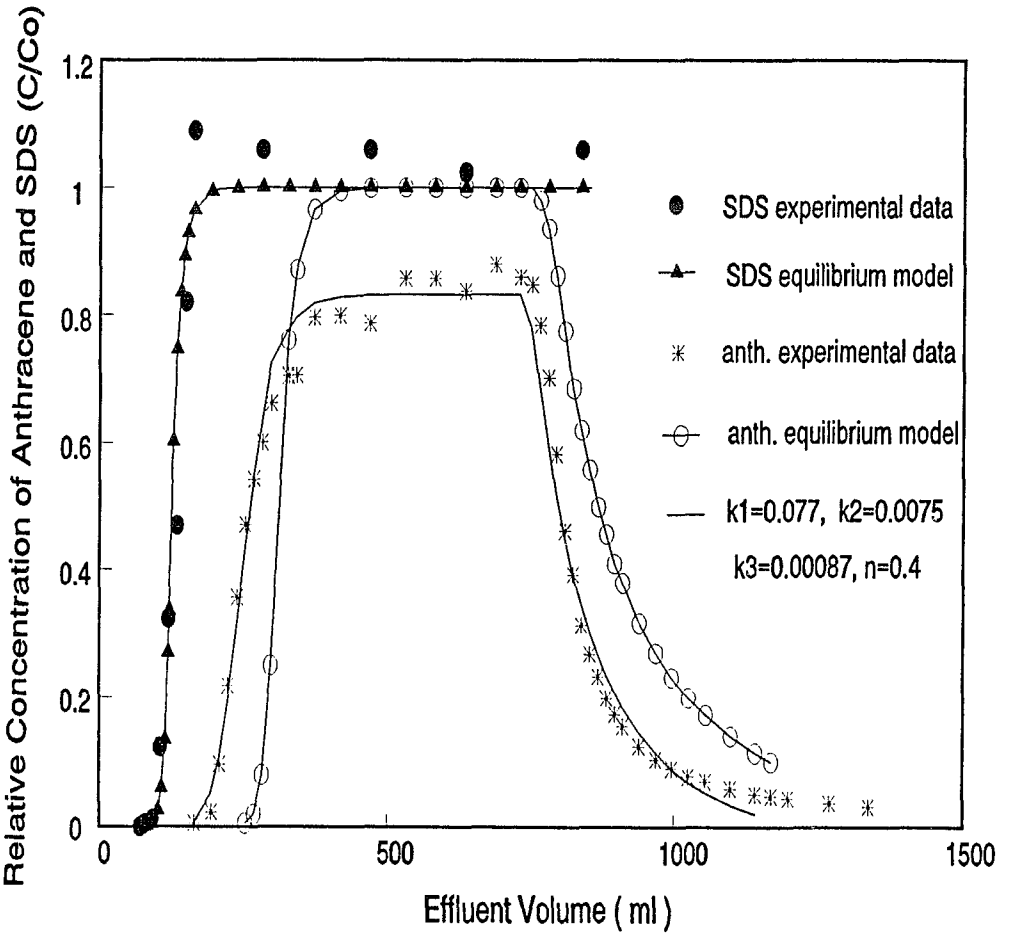

Figure 6.11 Column experiment I: data, SDS equilibrium model and anthracene non-equilibrium model (SDS Co = 30 mM , anth Co = 2.98 mg/l and b = 1.32 mg/l).

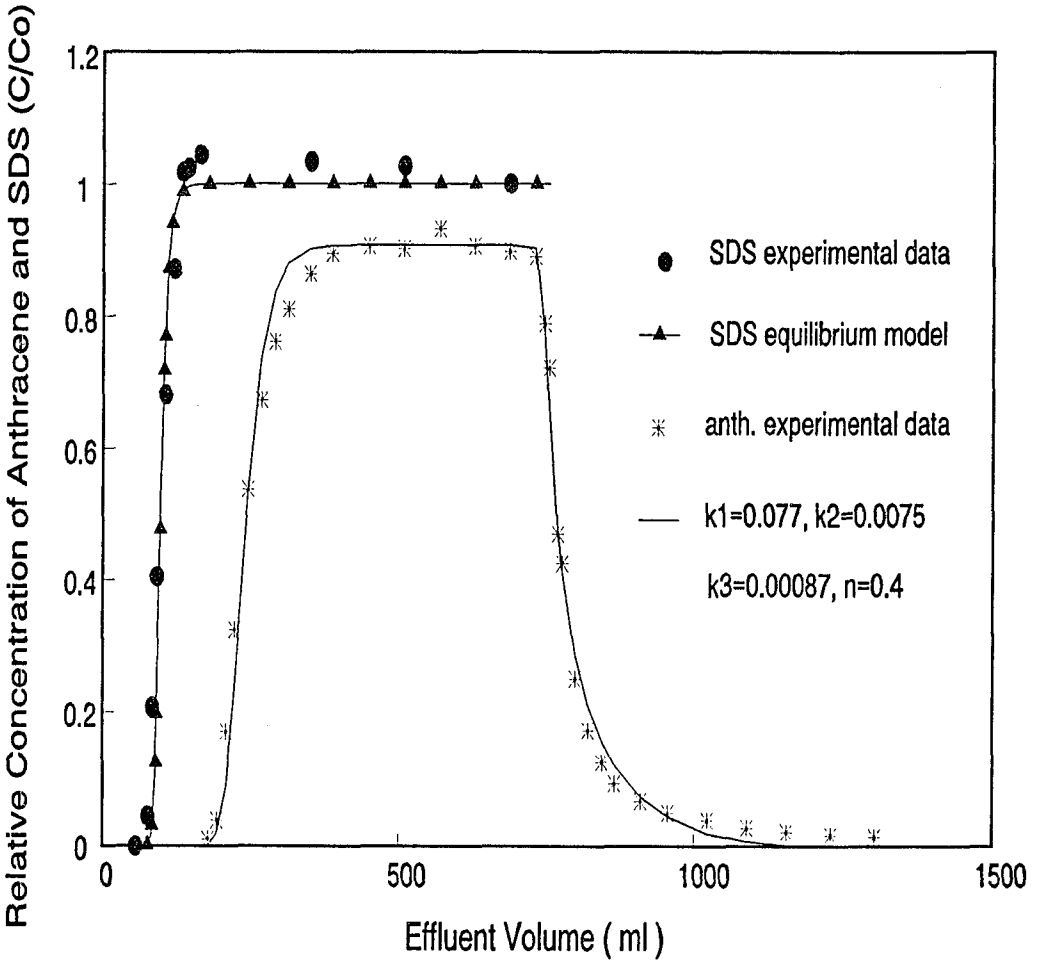

Figure 6.12 Column experiment II: data and the prediction of SDS and anthracene break through curves (SDS Co = 60 mM, anth Co = 7.87 mg/l and b = 2.02 mg/l).

anthracene present in SDS solution (data are presented in Chapter 5). Therefore, the native soil is the only reactive porous media which accounts for the 1/3 in the second term of the left hand side of the governing equation (6.5) of chemicals' transport because the mixed soil is at a weight ratio of 2 sand to 1 soil. Equation (6.5) can be further modified depending on whether or not the solute concentration in aqueous phase is in equilibrium with non-aqueous phase.

Since the surfactant is a hydrophilic compound, the equilibrium is established quickly and the mathematical equation for such condition can be expressed as

$$\frac{\partial S}{\partial t} = \frac{\partial S}{\partial C}\frac{\partial C}{\partial t} \tag{6.6}$$

where $\partial S/\partial C$ depends on the equilibrium isotherm $S = f(C)$. By substituting equation (6.6) in equation (6.5) one obtains

$$\frac{\partial C_{surf}}{\partial t}\left[\,1 + \frac{\rho\,(1-\theta)}{3\,\theta}\frac{\partial S_{surf}}{\partial C_{surf}}\,\right] = D_x\frac{\partial^2 C_{surf}}{\partial x^2} - v\frac{\partial C_{surf}}{\partial x} \tag{6.7}$$

Equation (6.7) is the mathematical model for the solute under equilibrium condition which is valid with two initial conditions:

$$S_{surf}(x,0)=0 \tag{6.7a}$$

$$C_{surf}(x,0)=0 \tag{6.7b}$$

and two boundary conditions:

$$C_{surf}(0,t) = \begin{cases} 0, & t \le T_{surf} \\ Co_{surf}, & t > T_{surf} \end{cases} \tag{6.7c}$$

$$\frac{\partial C_{surf}}{\partial x} = 0 \qquad x = L \; ; \quad t = t \qquad (6.7d)$$

where Co_{surf} is the concentration of inflow surfactant solution; T_{surf} is the time at which surfactant was pumped into the column; and L is the length of the column. The $\partial S_{surf}/\partial C_{surf}$ term can be calculated from equilibrium isotherm (equation 6.2) for a specific aqueous concentration of SDS. Finite different method is used to solve the batch equilibrium equation (6.2) and the column governing equation (6.7) simultaneously with the above initial and boundary conditions. The results of the modeling prediction on SDS are shown in Figure 6.11 (30 mM) and 6.12 (60 mM).

The equilibrium model has been tried to predict the anthracene break through curve in 30 mM SDS solution based on column governing equation (6.5) and equilibrium isotherm equation (6.3) (Figure 6.11) with following initial conditions and boundary conditions. The two initial conditions are

$$C(x,t<T_0) = 0 \qquad (6.5a)$$

$$S(x,t<T_0) = 0 \qquad (6.5b)$$

and the boundary conditions are

$$C(0,t) = \begin{cases} 0, & t < T_0 \; ; \; t > T_e \\ Co, & T_0 \leq t \geq T_e \end{cases} \qquad (6.5c)$$

$$\frac{\partial C}{\partial x} = 0, \qquad x = L \; ; \quad t = t \qquad (6.5d)$$

where T_0 is the time at which the surfactant solution with anthracene C_0 was introduced into the column; and T_e is the time at which the pure surfactant solution

was started again. Comparison of the equilibrium model prediction and the experimental data showed the characteristics of a non-equilibrium break-through curve, namely asymmetry, early occurrence and tailing.

Because of the failure of the equilibrium model to predict the experimental data for anthracene, it seems appropriate that a non-equilibrium model be applied to describe the anthracene transport through the columns. Under non-equilibrium conditions, the process is limited by the rate of reaction (Brusseau and Rao, 1989). Many researchers have expressed the reversible reaction using the Freundlich isotherm form as in equation (6.8) (Brusseau, 1992; Nkedi-Kizza et al., 1989; Hatfield and Stauffer, 1992) and the irreversible reaction, assuming to be a first-order, has been reported in the literature to be of the form as in equation (6.9) (Mansell et al., 1977; Amacher et al., 1988):

$$\frac{\partial S}{\partial t} = k_1 K C^{1/m} - k_2 S \qquad (6.8)$$

$$(1 - \theta) \rho \frac{\partial S}{\partial t} = \theta k_3 C \qquad (6.9)$$

where k_1, k_2, and k_3 are forward, backward and irreversible first-order reaction rates (T^{-1}), and K and m are the constants from Freundlich adsorption isotherm. Based on the experimental observations that, (a) the rate of anthracene adsorption was slow and (b) the aqueous anthracene concentration in desorption experiment decreased with the increase in the time of contact, it can be assumed that under general conditions both

of the above rate-limited reactions occur during the soil washing process. Therefore, the non-aqueous phase anthracene concentration can be expressed as

$$S = S_1 + S_2 \tag{6.10}$$

where S_1 is the concentration of anthracene in non-aqueous phase based on a reversible reaction and S_2 is the concentration of anthracene in non-aqueous phase based on an irreversible reaction. For the experimental condition used in this study, it was noted that the adsorption of anthracene is expressed by Langmuir isotherm. Therefore, the reversible reaction (equation 6.8) can be modified as

$$\frac{dS_1}{dt} = \frac{k_1 C}{b + C} - k_2 S_1 \tag{6.11}$$

and the irreversible reaction is expressed as

$$\rho \frac{(1-\theta)}{3} \frac{dS_2}{dt} = \theta k_3 C^n \tag{6.12}$$

where n is the reaction order. Finite different method is used to solve the equations (6.5), (6.10), (6.11) and (6.12) simultaneously with the initial and boundary conditions stated earlier for anthracene. The reaction order (n) and the rate coefficients (k_1, k_2 and k_3) are obtained by calibrating the non-equilibrium model using the experimental break-through data for anthracene C_o= 2.98 mg/l (30 mM SDS) for a minimum residue. The results are presented in Figure 6.10. The non-equilibrium model was verified by using those rate coefficients obtained from the first column experiment to predict the anthracene concentration of the second column experiment (C_o=7.87 mg/l and SDS = 60 mM). The experimental results shown in Figure 6.12

are in good agreement with the model predictions. It should be noted that the value of energy constant, b, used for the second column corresponds to that for 60 mM SDS concentration. Coefficients, constants and parameters used in column modeling are listed in Table 6.2.

Discussions

The dispersive coefficient in one-dimensional model represents the longitudinal hydrodynamic dispersion and can be expressed as a linear function of the pore velocity (Freeze and Cherry, 1979)

$$D = \alpha v + D^*$$

where α is a characteristic property of the porous medium (L) and D^* is the coefficient of molecular diffusion (L^2/T). This relationship was verified using the results of Cl^- tracer experiment (Figure 6.3). The dispersive coefficients obtained by using this relationship were used for the modeling and predicting SDS and anthracene concentrations. Although SDS and anthracene molecules are different from chloride ions, the coefficients were observed to work well. This observation can be explained due to the fact that under the experimental conditions the main factors influencing the dispersive coefficient are the pore velocity and the properties of the porous medium rather than the molecular diffusion.

The results presented in the first region of Figure 6.4 show that the loss of surfactant increases with an increase in surfactant concentration. A maximum loss of surfactant from the aqueous phase occurs when the aqueous phase surfactant

Table 6.2 The modeling parameters of column experiments

Items	Column I		Column II	
	SDS	Anth	SDS	Anth
Co mg/l	8651	2.98	17303	8.78
v cm/min	0.0070	0.0070	0.0074	0.0074
D cm^2/min	0.0015	0.0015	0.00151	0.00151
Δt min	3.0	3.0	3.0	3.0
Δx cm	0.1	0.1	0.1	0.1
L cm	3.0	3.0	3.0	3.0
θ	0.48	0.48	0.48	0.48
ρ kg/l	2.5	2.5	2.5	2.5
n	--	0.4	--	0.4
b mg/l	--	1.32	--	2.02
k_1 mg/kg/min	--	0.056	--	0.056
k_2 min^{-1}	--	0.0045	--	0.0045
k_3 min^{-1}	--	0.00033	--	0.00033

concentration reaches the CMC level. An increase in aqueous phase surfactant concentration beyond the CMC level results in a decreasing trend of non-aqueous phase surfactant concentration which finally levels off.

The relationship between the aqueous and non-aqueous phase surfactant concentration is controlled by the physical forms of the surfactant molecules. If the surfactant concentration of the aqueous phases is below the CMC, the surfactant molecules will exist as monomers and the hydrophobic tails of the monomers tend to orient themselves away from the water molecules. Thus, in monomer form, the surfactant molecules are adsorbed by the soil particles. The precipitation of divalent ions dodecylsulfate may be the other reason for the increase of the non-aqueous phase SDS concentration. The solubility product constant (K_{sp}) of $Ca(DS)_2$ is quit low, 5.02×10^{-10} (Stellner and Scamehorn, 1989). The sodium ions from SDS undergoing exchange with the exchangeable calcium and magnesium ions of soil release divalent ions which form complexes with the DS^- and induce precipitation resulting in a higher loss of surfactant. As the aqueous SDS concentration increases, the amount of adsorption and precipitation increases up to the CMC. At this concentration, micelles begin to form, and the DS^- molecules in micelles are oriented in such a way that the hydrophobic tails are surrounded by a layer of their negatively charged hydrophilic head groups and the tails are unable to come in contact with the soil particles. Therefore adsorption decreases due to the repulsion between the like charges of the head groups and the clay particles. As the aqueous SDS concentration increases, the negative charge of the micelle increases due to an increase in the aggregation number.

This increases the repulsion between the micelles and the clay particles resulting in less adsorption. Thus, as the level of surfactant increases beyond the CMC, adsorption of aqueous surfactant molecules on soil particles decreases and eventually levels when the aggregate number of micelles reaches their maximum value. Because of the micellization of SDS solution, the equilibrium curve fitting is divided in three regions. Below CMC the loss is a linear function of aqueous surfactant concentration. Above CMC the loss decreases exponentially and at very high level above CMC the loss is constant.

MaClntyre and his coworkers (1991) found a good agreement on the batch experiments and column experiments among the fast sorption kinetics and linear isotherms. In this work we found that the equilibrium model is a suitable model for SDS break-through curve although the equilibrium isotherm is not linear all the time. The equilibrium of SDS with soil usually only takes a few hours (Matthijs and De Henau, 1985). The retention time of the solution in columns was about 10 hours and the concentration of SDS solution in this experiment was very high leading to rapid establishment of the equilibrium condition. When the effluent SDS concentration predicted by the model reaches 100% of the inflow SDS concentration, the observed surfactant concentrations in the effluent are higher than the predicted values (Figure 6.11 and 6.12). This problem may be caused by measurement errors. The measurable range of SDS by the standard method is up to 3 mg/l, the effluent samples have to be diluted 10,000 times when they reach 100% of inflow and a small reading error will be greatly enlarged. The yellow color observed in the effluent samples

caused by the organic matter in the soil interferes with the UV spectrophotometer's reading for SDS measurement. However, most of the relative reading errors are within 5%.

Hydrophobic organic compounds are typically partitioned in either aqueous phase or soil organic materials (Dzombak and Luthy, 1984; Chiou, 1983; Karickhoff et al., 1979; Lion et al., 1990). Hydrophobic adsorption can also be driven by the incompatibility of the non-polar compounds with water (Westall, 1987). The existence of surfactant will affect the equilibrium of hydrophobic adsorption. Anthracene adsorption in SDS solution takes a long time and the isotherm is a Langmuir type, that is, monolayer adsorption. The quasi-equilibrium isotherms of anthracene in 30 and 60 mM SDS solutions (equations 6.3 and 6.4) have same ultimate adsorption capacities (the A term), which explains that for this soil the maximum adsorption per unit soil is limited and it is not a function of SDS concentration. However, the values of energy constant (the b term) are different in equations (6.3) and (6.4), which implies that the SDS concentration affects the stability of anthracene in solution. Higher concentration of SDS yields a higher value for b implying stability for anthracene in SDS solution. However, the values of b in 30 and 60 mM SDS solution are still of the same order and anthracene still has a strong tendency to leave the solution because of its high hydrophobicity.

The non-singularity of anthracene adsorption and desorption tells us that besides the partition between the soil organic matter and SDS solution, there are other irreversible reactions. Such non-singularity phenomenon has been reported in the

literature by many investigators and are reviewed by Brusseau and Rao (1989). It is possible that after a long time of contact the chemical or biological interactions between anthracene and soil form measurably slow reversible or irreversible components. From the HPLC analysis it was noticed that the number of peaks other than the anthracene increased after a long time of reaction. Based on these observations, it is reasonable to assume that more than one and at least two reactions are going on. One reaction is reversible in nature and related to the quasi-equilibrium condition and the other is irreversible related to the anthracene concentration and reaction time.

Since anthracene needs a long time to reach the quasi-equilibrium and non-linear, the equilibrium model is not suitable. From the Figure 6.11 we can see that the line from the equilibrium model is lag to the experimental data and reaches 100 percent very quickly. However, as for column experiments, sometimes the asymmetry of break-through curve is caused by hydrodynamic dispersion (Brusseau and Rao, 1989). The Peclet number ($P = vL/D$) measures the magnitude of hydrodynamic dispersion. In our cases the value of P are 67 and 70 (> 10) and the possibility of hydrodynamic dispersion-related asymmetry can be eliminated. Therefore, rate-limited non-equilibrium is the main reason for the asymmetry. As matter of fact the anthracene concentrations have never been 100 percent in either column experiment, which means that the irreversible reaction is very important to the model. The experimental data showed clear evidence of early solute arrival, asymmetry, and tailing, which contribute to rate-limited coefficients and the energy

constant. The sensitivity analysis of energy constant (b), reaction order (n) and rate coefficients are shown in Table 6.3. The coefficients from the minimum residue are increased or decreased 20 % individually, and then the new residues are calculated and compared with the minimum residue. The rate coefficients, k_1 and k_2, are the most sensitive coefficients and the reaction order is the least sensitive coefficient for this experiment.

The prediction of anthracene break-through curve in 60 mM SDS solution is made by the non-equilibrium model and using the independently measured constant and coefficients such as the energy constant (b), from batch isotherms, dispersive coefficient (D_x) from the tracer experiments, and rate coefficients (k_1 , k_2 and k_3) as well as reaction order (n) from the first column experiment (Figure 6.11). The model is verified and found to produce a good break-through curve prediction.

Summary

In soil washing by surfactant, the transport and fate of chemicals are dependent on the interactions among soil, anthracene, surfactant, and the hydrodynamic conditions of the matrix. The transport of SDS can be predicted by an equilibrium model and the equilibrium isotherm is related to the micellization of SDS solution and soil properties. The SDS concentration will affect the stability of anthracene in the SDS solution. The quasi-equilibrium isotherm of anthracene adsorption in SDS solution is in the Langmuir isotherm form. The process of anthracene adsorption and desorption on the soil is a rate-limited process when anthracene is in SDS solution. Non-equilibrium model is suitable for the transport of anthracene in SDS solution.

Table 6.3 The sensitivity test of coefficients and constant (column I)

ΔR^2 %	R^2 E-3	n	b	k1	k2	k3
0	1.834	0.4	1.32	0.077	0.0075	0.00087
+1.1	1.854	0.48	"	"	"	"
+0.5	1.843	0.32	"	"	"	"
+185	5.235	0.4	"	0.092	"	"
+237	6.178	"	"	0.062	"	"
+164	4.850	"	"	0.077	0.009	"
+258	6.573	"	"	"	0.006	"
+29.1	2.367	"	"	"	0.0075	0.00104
+28.6	2.359	"	"	"	"	0.0007
+57.9	2.895	"	1.06	"	"	0.00087
+11.6	2.047	"	1.58	"	"	"

Notes: Column I: N = 38;

$R^2 = \Sigma(Y - Y^*)^2/N$

$\Delta R^2\% = 100\% (R^2-1.834)/1.834$

The prediction of transport of SDS and anthracene can be made based on independently measured parameters.

CHAPTER 7
CONCLUSIONS

A considerable amount of research has shown that soil washing by surfactants is a successful alternative to improve the effectiveness of pump-and-treat technologies for removing hydrophobic organic compounds. A review of soil washing using surfactants indicates a lack of understanding and prediction of the processes. Few studies have addressed the transport and fate of the contaminants and surfactants and little or no information is available on what interactions occur inside the soil matrix and how they affect the various processes. In this study, the understanding of the interactions among surfactant, contaminant and soil are based on one surfactant (SDS), one contaminant (anthracene) and one type of soil. In the absence of field tests, the models of transport and fate of contaminants are based on laboratory experiments. The selection of a surfactant is an essential concern to the effectiveness of contaminant removal. The transport and fate of chemicals are mainly dependent on the factors: the properties of soil, surfactant and chemicals, the interactions among them, and the hydrodynamic conditions of the soil matrix.

Surfactant selection for soil washing should be made with consideration not only of surfactant properties i.e. biodegradability, reusability, low CMC, and minimum adsorption of surfactant, but also on the interactions between the surfactant and the soil matrix. Soil-surfactant interactions leading to ion exchange, precipitation, adsorption and hydraulic conductivity changes should be considered while selecting a particular type of surfactant. Our results suggest that soil washing using SDS would

be suitable for the type of soil which contains less than 10 % clay. In such a case, the SDS solution can be efficiently passed through the matrix and still be eluted by water. Based on the results of the batch and column experiments, the following specific conclusions can be drawn on the interactions between soil and SDS and hydraulic conductivity changes:

- SDS loss on sand is negligible. The maximum loss of the anionic surfactant on the soil appears to be in the region of the critical micelle concentration (CMC) with or without the presence of sodium chloride.
- The equilibrium isotherm with soil shows that below the CMC the anionic surfactant loss increases as the surfactant concentration of aqueous phase increases. Above the CMC, the anionic surfactant loss will decrease and eventually level off.
- The transport of SDS through a column can be predicted by an equilibrium model.
- The loss of an anionic surfactant on soil increases in the presence of monovalent salts.
- The precipitation of the divalent electrolyte dodecylsulfate appears to be the prevalent mechanism influencing the change in hydraulic conductivity.
- The change in hydraulic conductivity is affected by soil composition when SDS is used.
- The rate of change in hydraulic conductivity is also affected by the concentration of SDS solution until exchangeable calcium becomes limiting.

Surfactant solutions can greatly decrease the interfacial tension and increase the solubility of hydrophobic organic compounds. Therefore, surfactant solutions enhance the mobilization of hydrophobic organic compounds. Below the CMC, the increase of the surfactant concentration will greatly decrease the surface tension of the solution but will not affect the solubility of hydrophobic compounds. Above CMC, the solubility of hydrophobic compounds is a linear function of surfactant concentration. The maximum solubility or limited solubility of anthracene increases linearly with the increase in SDS concentration when SDS concentration is above the CMC level. On the aspect of interactions between hydrophobic organic compounds and soil, hydrophobic adsorption is driven not only by the attraction of the organic matter in soil, but also by the incompatibility of the non-polar compounds with water. Because of the hydrophobic core of micelles, the stability of hydrophobic organic compounds in solution is increased. The transport and fate of hydrophobic organic compounds will depend on soil properties, surfactant concentration, and the different removing mechanisms. When the soil matrix is fine sand, the following specific conclusions can be drawn:

- Anthracene cannot be effectively removed by water or surfactant solution at a concentration less than or equal to the CMC.
- When anthracene is in SDS solution, the adsorption of anthracene on sand is negligible.

- Solubilization is the main mechanism for the removal of anthracene from the contaminated sand, and the limited solubility of anthracene in SDS affects the removal rate when anthracene contamination is high.
- The kinetics of anthracene solubilization from contaminated sand into surfactant solution can be expressed using the exponential Elovich equation.
- The mixing-cell concept is a reliable and simple numerical method to simulate the sand washing process.
- SDS, an anionic surfactant, can be successfully used to solubilize hydrophobic organic compounds, such as anthracene, from saturated sandy environments under dynamic conditions.

When the soil matrix is composed of sand and soil, soil organic matter attracts the hydrophobic organic compounds and clay minerals react with the surfactant and provide a large surface area for adsorption. The performance of hydrophobic organic compounds on soil is different from that on fine sand. The following specific conclusions can drawn based on the conducted experiments with pure soil and a mixture of sand and soil:

- The concentration of SDS will affect the stability of anthracene in the SDS solution.
- The quasi-equilibrium isotherm of anthracene adsorption in SDS solution is a Langmuir isotherm form.
- The process of anthracene adsorption and desorption on soil is a rate-limited process when anthracene is in SDS solution. A non-equilibrium model gives

a good agreement for the fate and transport of anthracene in SDS solution for column experiments.

- The prediction of anthracene transport in column experiments can be made based on independently measured parameters.

CHAPTER 8
RECOMMENDATIONS FOR PRACTICAL APPLICATION AND RESEARCH

Based on the findings of this study it seems to be appropriate to undertake further research in the following areas:

- The foundation of surfactant soil washing is based on the concept of using surfactant enhanced mobilization of hydrophobic contaminants. However, surfactants also creates the potential of migrating the contamination. Especially when the contaminants are heavier than water, the downward movement may contaminate another aquifer. Besides the laboratory experiments on surfactant selection, adsorption and desorption etc., other factors such as hydrogeological investigation, extraction well locations, and pumping rates are also vital considerations of a successful treatment.
- One of the limitations of surfactant soil washing is the cost of surfactants. Recovery and reuse of surfactants will strongly help to decrease the cost of surfactant soil washing. Soil washing research should be expanded in this area to make the whole system more efficient.
- Unlike laboratory experiments, most field sites are heterogeneous with a low permeability zone. The pumping liquid often follows preferential paths in areas of high permeability. The slow rate of diffusion through the low permeability zone to preferential flow may cause steady and low level removal even when a surfactant solution is used to enhance the efficiency. Prediction models should base on the real field conditions.

- Continuous flow was used in all column experiments of this study. The pulsing method of pumping surfactants may help to increase the concentration of chemicals in surfactant solution, which will lower the overall cost because less surfactant solution is needed.
- Although surfactants are very hydrophilic and water will be suitable to elute it out of subsurface environments, it is possible to have a long tailing because of low permeable zone. Biodegradation may be a better choice to cleanup the the surfactant and contaminant when they are in low concentration.
- The degree of biodegradation is an important criteria of surfactant selection. Biodegradation of surfactants may create a clogging problem which will narrow pore space or stop flow.

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APPENDIX A:

EXPERIMENTAL SETUPS

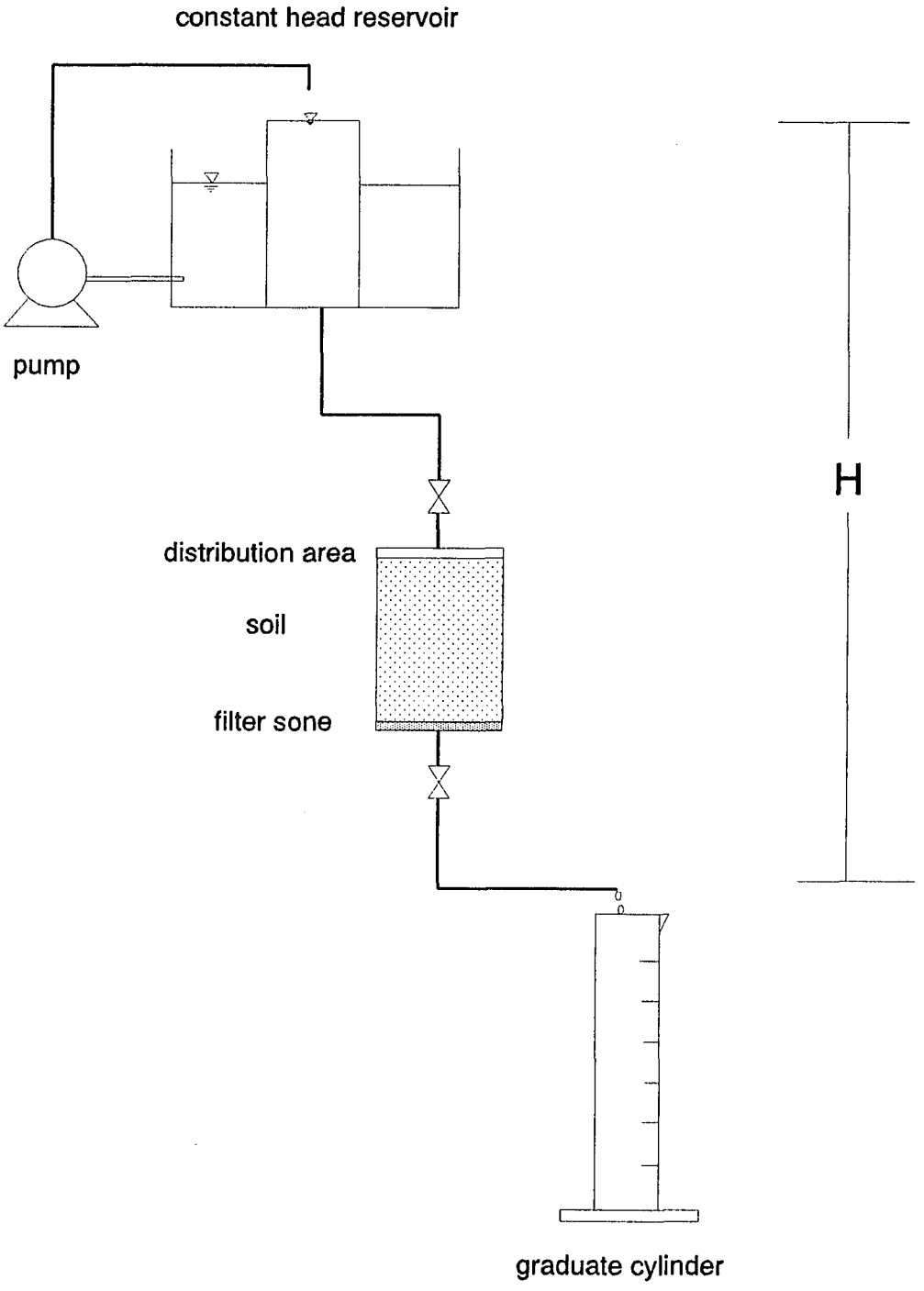

Figure A.1 Experimental setup for hydraulic conductivity.

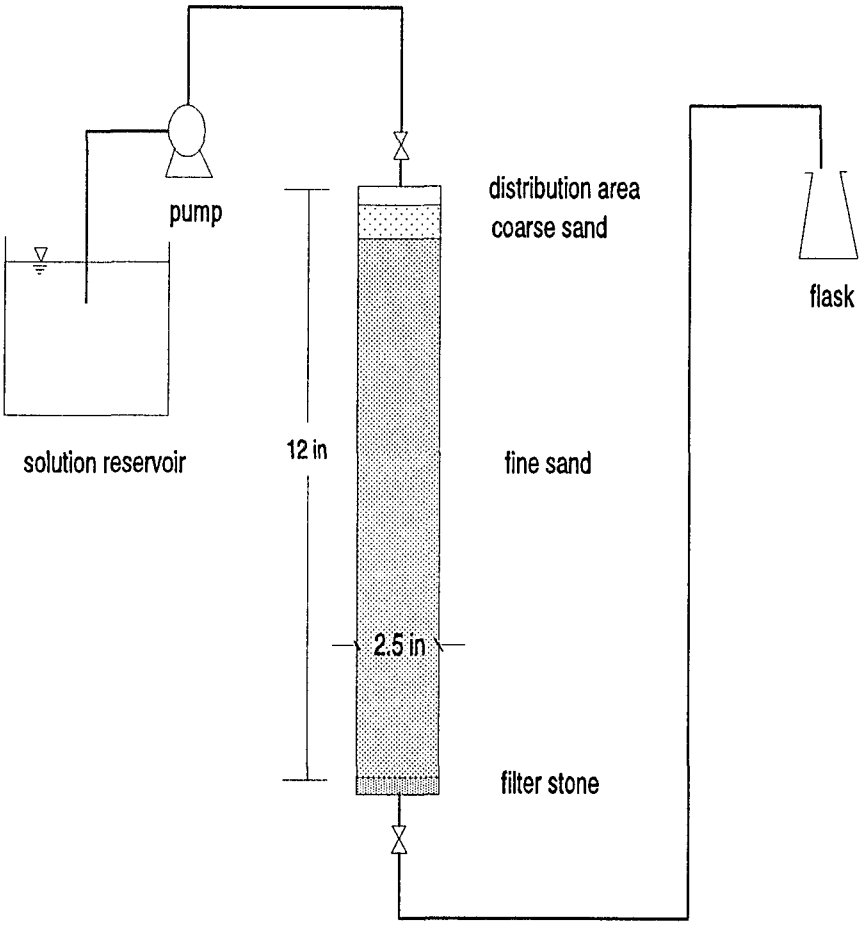

Figure A.2 Experimental setup for sand columns.

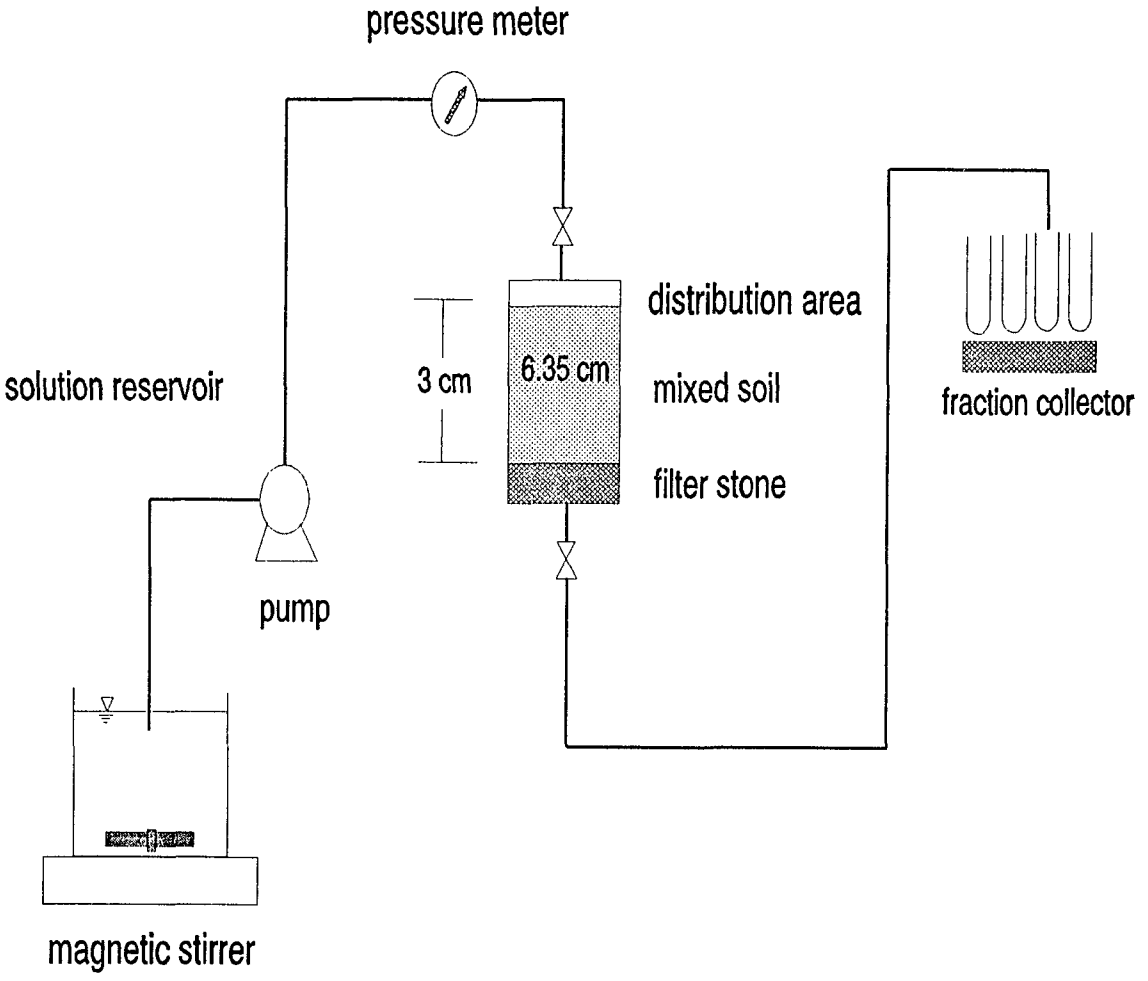

Figure A.3 Experimental setup for mixed soil columns.

APPENDIX B:

CALIBRATION CURVES

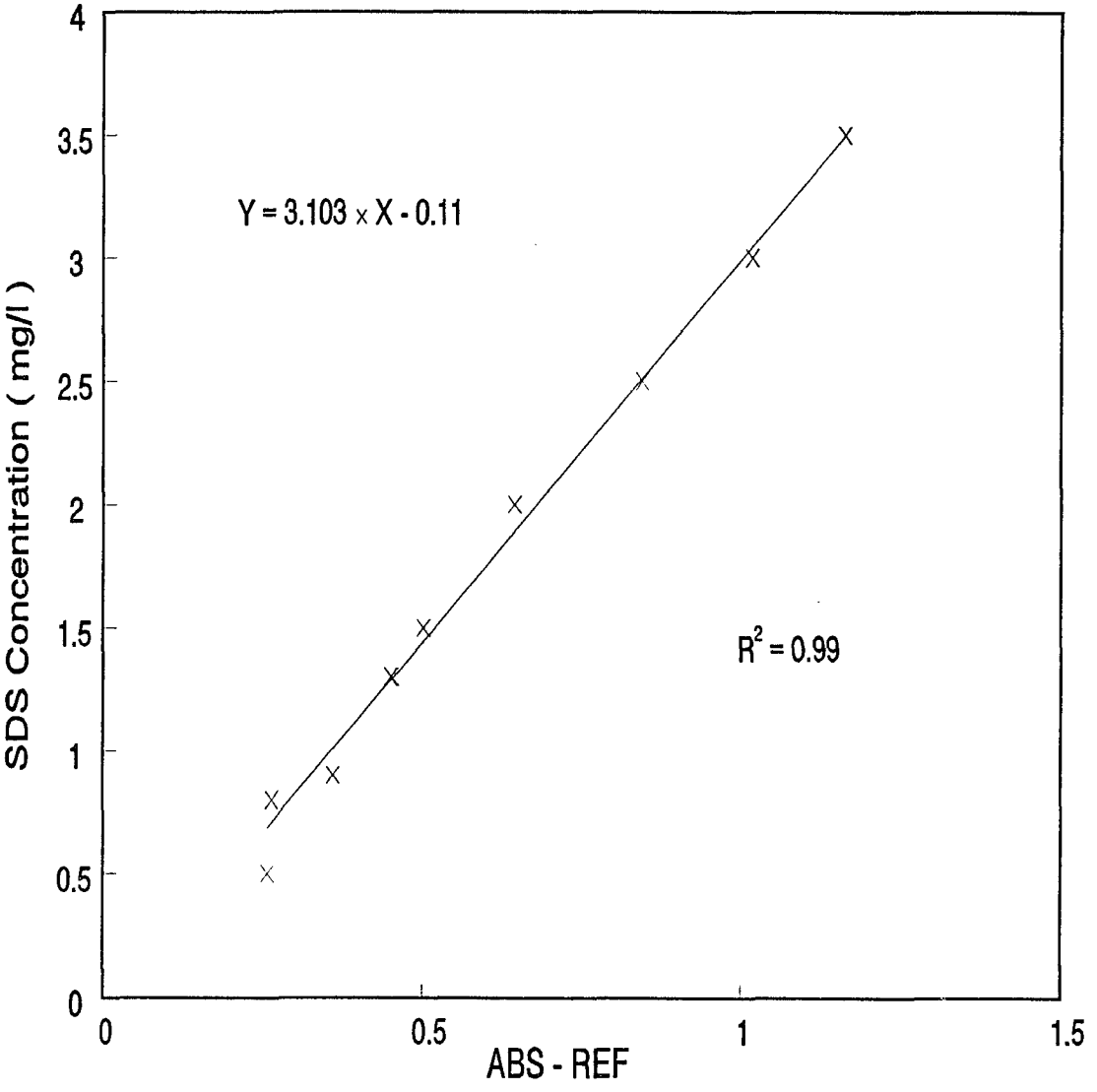

Figure B.1 SDS calibration curve using UV/VIS spectrophotometer (analytical wavelength = 652 nm, reference wavelength = 720 to 800 nm, integration time = 1 second and the solvent is chloroform).

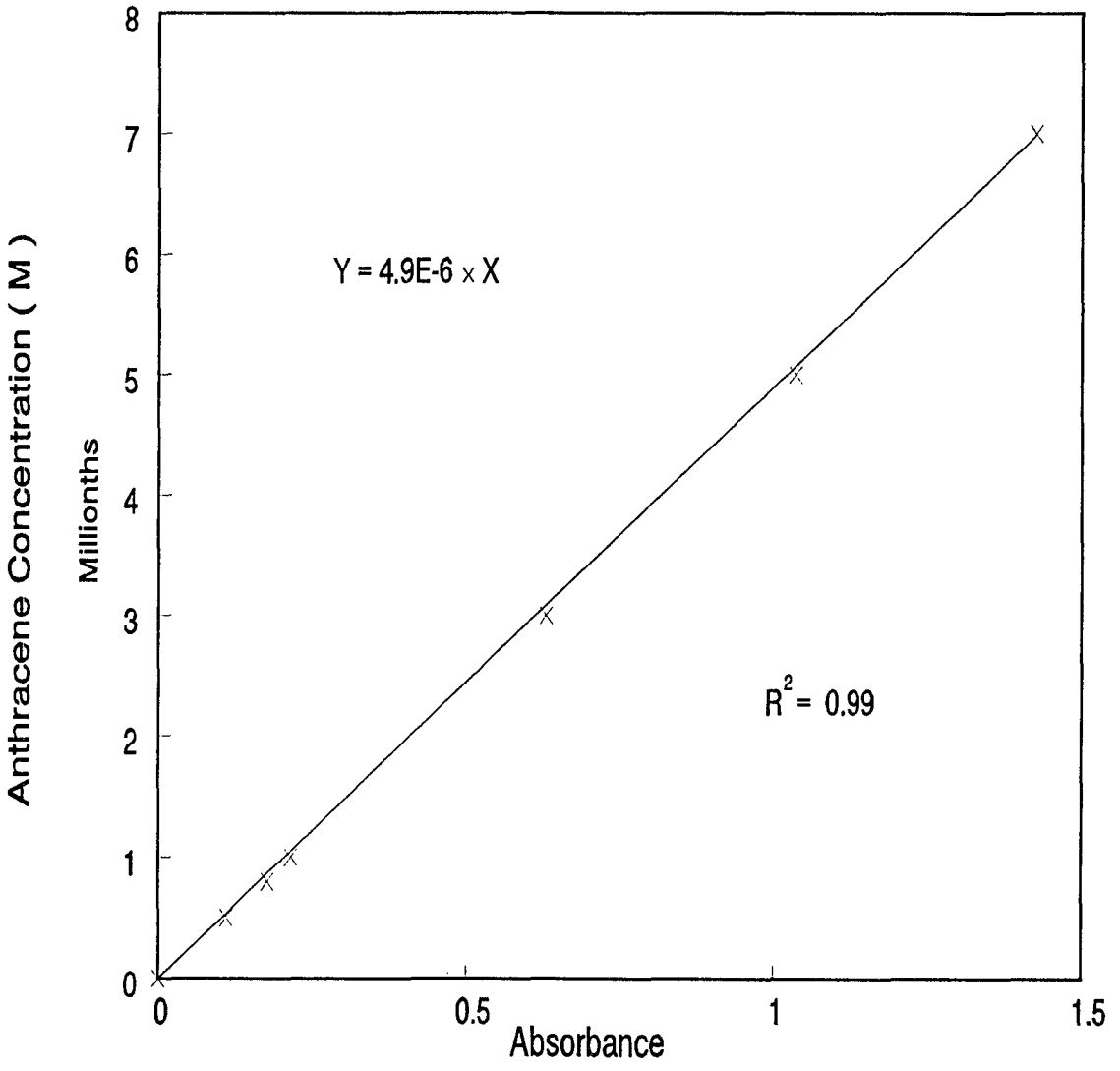

Figure B.2 Anthracene calibration curve using UV/V spectrophotometer (analytical wavelength = 252 nm, integration time = 1 second and the solvent is alcohol).

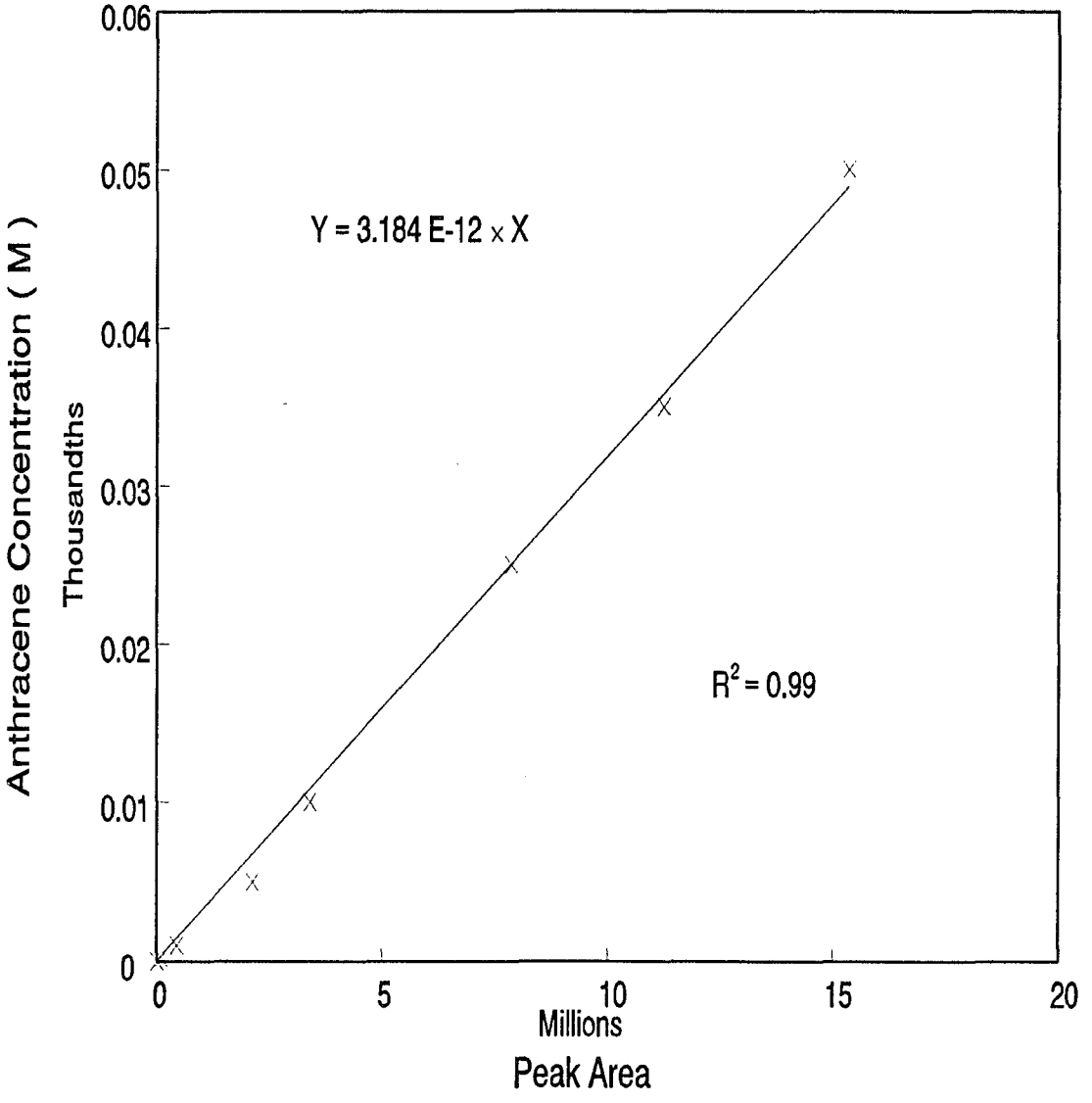

Figure B.3 Anthracene calibration curve using HPLC (signal wavelength = 250 to 260 nm, reference wavelength = 400 to 480 nm, response time = 1 second and the solvent is alcohol).

APPENDIX C:

COMPUTER PROGRAMS

Mixing-cell Method

```
c
c       Program name is mix.for.  The output file is mw.dat.
c       This is mixing-cell concept for SDS and anthracene concentrations
c       of contaminated sand column experiments.
c       Solve equations (5.13), (5.15), (5.16) and (5.18).
c       ------------------------------------------------------------------------
c       c - anthracene concentration; c1 - SDS concentration
c       cs - limited solubility;
c       v1=0.368 cm/min; v2=0.558 cm/min
c       porosity=0.3; dt=5 min; dx=5 cm; L=12 in; d=2.5 in
c       MW of anthracene=178.24; cs in water=0.073 mg/l
c       ------------------------------------------------------------------------
        dimension c(7,212), c1(7, 212), cs(7,212), c3(18), c4(18)
        open (unit=6, file='mex.dat', status='new'
c
c                       ---     initial condition of SDS   ---
        do 100 i=2,7
 100    c1(i,1)=0.0
c                       ---     boundary conditions   ---
        do 105 i=2,132
 105    c1(1,i)=60.0
        do 106 i=133,180
 106    c1(1,i)=0.0
        do 107 i=180,212
 107    c1(1,i)=60.0
        c1(1,1)=60.0
c                       ---     surfactant distribution   ---
        do 130 i=2,7
              do 110 j=2,132
 110          c1(i,j)=c1(i,j-1)+0.364*(c1(i-1,j-1)-c1(i,j-1))
              do 120 j=133,212
 120          c1(i,j)=c1(i,j-1)+0.558*(c1(i-1,j-1)-c1(i,j-1))
 130    continue
c                       ---     calculate cs  ---
        do 160 i=2,7
              do 150 j=2,212
                    if (c1(i,j).lt.8.0) goto 140
                    cs(i,j)=(.41+1.19*(c1(i,j)-8.0)*0.17824
                    goto 150
 140                cs(i,j)=0.073
 150          continue
 160    continue
```

```
c                    ---     initial condition of anthracene   ---
      do 10 i=2,7
 10   c(i,1)=0.073
c
c                    ---     boundary condition of anthracene   ---
      do 20 i=2,212
 20   c(1,j)=0.0
      c(1,1)=0.0
c                    ---     calculate anthracene concentration   ---
      do 70 i=2,7
            k=1
            do 60 j=2,212
                  if (j.le.132) goto 30
                  c(i,j)=c(i,j-1))+0.588*(c(i-1,j-1)-c(i,j-1))+2650*2.33*.0213/k
                  goto 40
 30               c(i,j)=c(i,j-1))+0.364*(c(i-1,j-1)-c(i,j-1))+2650*2.33*.0213/k
 40               if (c(i,j).gt.cs(i,j)) goto 50
                  k=k+1
                  goto 70
 50               c(i,j)=cs(i,j)
 60          continue
 70   continue
c                    ---     c mg/l to mM  and write in the end of every hour ---
      do 80 i=1,7
            do 80 j=1,212
 80   c(i,j)=c(i,j)/0.17824
      do 90 j=12,212,12
 90   write (6,200) (c(i,j), i=1,7)
 200  format(8f.10.5)
c                    ---     calculate the average concentration   ---
      do 220 i=1,18
            w=0.0
            j=(i-1)*12+1
            jj=i*12
            do 210 ll=j,jj
 210        w=w+c(7,ll)
 220  c(3)=w/12.0
c                    ---     transfer mM to mg/hour removal   ---
      do 230 i=1,11
 230  c3(i)=c3(i)*0.03743
      do 240 i=12,18
 240  c3(i)=c3(i)*0.05668
```

```
c                    ---     calculate removal percentage and write  ---
      do 260 i=1,18
            w=0.0
            do 250 k=1,i
250         w=w+c3(k)
260   c4(i)=w
      do 270 i=1,18
270   c3(i)=(300.8-c4(i))/300.8*100.0
      write (6,200) (c3(i), i=1,18)
      stop
      end
```

Equilibrium Model for SDS Column

```
c
c     Program name is mw1sds.for.  The output file is mw1.dat.
c     This is equilibrium model for SDS concentration of column experiments.
c     Solve equations (6.7) and (6.14) by central finite different method.
c     ------------------------------------------------------------------------------
c     dt - time step;  dx - x coordinate step;  nx - total steps
c     hold, hnew - old and new concentrations of SDS
c     s, ss - retardation factor; c1, c2 --  dispersive and advective items
c     v - pore velocity; d - dispersive coefficient
c     hh1 -- average conc./hour; hh2 -- effluent volume
c     porosity = 0.48; section area = 31.669; total length = 3
c     MW of SDS = 288.38
c     ------------------------------------------------------------------------------
c
      dt=3.0
      dx=0.1
      d=0.0015
      v=0.1065/31.669/0.48
      nx=31
      nlx=nx-1
      kount=1
      kprint=10
      nend=900
      s=2500.0*(1.0-0.48)/0.48/3.0*0.00555+1.0
c           ---     boundary condition  ---
      hold(1)=30.0*288.38
      hnew(1)=30.0*288.38
c           ---     initial condition  ---
      do 10 i=2, nx
            hold(i)=0.0
            hnew(i)=0.0
```

```
 10     continue
c               ---     calculation   ---
       do 50 n=1, nend
               do 20 i=2, nlx
                       c1=(hold(i+1)-2.0*(hold(i)+hold(i-1))*d/dx/dx
                       c2=v*(hold(i+1)-hold(i-1))/2.0/dx
                       if (hold(i).le.2295.0) goto 15
                       hnew(i)=hold(i)+(c1-c2)*dt
                       if (hold(i).le.2315.0.or.hold(i).gt.12580.0) goto 20
                       step=0.00105*exp(-0.000089*(hold(i)-2307))
                       ss=(2500.0*(1.0-0.48)/0.48)*step/3.0+1.0
                       hnew(i)=hold(i)+(c1-c2)*dt/ss
 15                    hnew(i)=hold(i)+(c1-c2)*dt/s
 20            continue
               do 30 i=1,nlx
                       hold(i)=hnew(i)
                       hold(nx)=hold(nx-1)
                       if (hold(i).le.0.0) hold(i)=0.0
 30            continue
               if (kount.ne.kprint) goto 45
               kount=0
 45            time= time+dt
               kount=kount+1
               hh(n)=hold(nx)
 50    continue
c               ---     calculate the average concentration/hour   ---
       do 70 i=1,45
               w=0.0
               do 60 j=1,20
 60            w=w+hh(j+(i-1)*20)
               hh1(i)=w/20
 70    continue
c               ---     calculate the responded effluent volume   ---
       do 80 i=1,45
 80    hh2(i)=i*60*.1065
c               ---     write to output file   ---
       write (6,90)
 90    format(1h1, 20x,'concentration mg/l',20x,'effluent volume ml',//)
       do 100 i=1,45
 100   write (6,*) hh1(i),hh2(i)
       stop
       end
```

Non-equilibrium Model for Anthracene Column

```
c
c       Program name is mw12.for.  The output file is mw1.dat.
c       This is non-equilibrium model for anthracene concentration of column
c       experiments.
c       Solve equations (6.13), (6.10), (6,11) and (6,12) by central finite different
c       method.
c       ------------------------------------------------------------------------------------
c       dt - time step;  dx - x coordinate step;  nx - total steps
c       hold, hnew - old and new relative concentrations of anthracene in aqueous
c       phase
c       sold, snew - old and new concentrations of anthracene in non-aqueous phase
c       v - pore velocity; d - dispersive coefficient
c       hh1 -- average conc./hour; hh2 -- effluent volume
c       porosity = 0.48; section area = 31.669; total length = 3
c       ek1,ek2,ek3 - rate constants; b - energy constant
c       c1,c2 - dispersive and advective items; c3,c4 - reaction items
c       ------------------------------------------------------------------------------------
c
        dt=3.0
        dx=0.1
        d=0.0015
        ek1=0.077
        ek2=0.0075
        ek3=0.00087
        v=0.1065/31.669/0.48
        z=2.5(1.0-0.48)/0.48/3
        nx=31
        nlx=nx-1
        kount=1
        kprint=10
        nend=3600
c                       ---     boundary condition of C before Co=0   ---
        hold(i)=2.98
        hnew(i)=2.98
c                       ---     initial condition   ---
        do 10 i=2,nx
              hold(i)=0.0
              hnew(i)=0.0
              sold(i)=0.0
              snew(i)=0.0
10      continue
```

```
c                    ---     calculation   ---
      do 50 n=1,nend
            u=float(n)
            if (n.gt. 1745) goto 501
c                          boundary condition of S
            sold(1)=0.693*ek1/ek2*(1.0-exp(-ek2*dt*u))
            snew(1)=sold(1)
            goto 502
c                    ---     boundary condition after Co=0   ---
 501        hold(1)=0.0
            hnew(1)=0.0
            sold(1)=0.0
            snew(1)=0.0
c                    ---     continue of calculation part   ---
 502        do 20 i=2,nlx
                  c1=(hold(i+1)-2.0*(hold(i)+hold(i-1))*d/dx/dx
                  c2=v*(hold(i+1)-hold(i-1))/2.0/dx
                  z1=(ek1*hold(i)/(b+hold(i))
                  z2=ek2*sold(i)
                  c3=z*(z1-z2)
                  if (hold(i).le.0.0) goto 21
                  c4=ek3*hold(i)**0.4
                  goto 22
 21               c4=0.0
 22               hnew(i)=hold(i)+(c1-c2-c3-c4)*dt
                  snew(i)=sold(i)+(z1-z2)*dt
 20         continue
            do 30 i=1,nlx
                  hold(i)=hnew(i)
                  sold(i)=snew(i)
                  hold(nx)=hold(nx-1)
                  if (hold(i).le.0.0) hold(i)=0.0
 30         continue
            if (kount.ne.kprint) goto 45
            knout=0
 45         time= time+dt
            kount=kount+1
            hh(n)=hold(nx)
 50   continue
c           ---     calculate the average concentration/hour   ---
      do 70 i=1,180
            w=0.0
            do 60 j=1,20
```

```
 60                  w=w+hh(j+(i-1)*20)
               hh1(i)=w/20/2.98
 70    continue
c              ---     calculate the responded effluent volume   ---
       do 80 i=1,180
 80    hh2(i)=i*60*0.1065/0.9+98.525
c              ---     write to output file   ---
       write (6,90)
 90    format(1h1, 20x,'concentration mg/l',20x,'effluent volume ml',//)
       do 100 i=1,150
 100   write (6,*) hh1(i),hh2(i)
       stop
       end
```

APPENDIX D

LETTER OF PERMISSION

SME

A member society of the American Institute of Mining, Metallurgical, and Petroleum Engineers, Inc.

May 25, 1993

Minwen Liu
Department of Civil Engineering
Louisiana State University
Baton Rouge LA 70803

Dear Mr. Liu:

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VITA

Minwen Liu was born January 21, 1957 in Shanghai, China. In 1978, the year China restored the entrance-exam after the Cultural Revolution, she began four years of study at Tongji University, Shanghai. Her undergraduate major was Water Supply and Sewerage. After college she worked two and half years as a teaching assistant and consultant. Then she spent two and half years for her Master of Engineering degree in Environmental Engineering at Tongji University. Her thesis topic was municipal sludge dewatering. Following graduation she worked as a college lecturer teaching various courses on wastewater treatment for two and half years. In 1989 she came to LSU to pursue a Ph.D. degree under the direction of Professor Dipak Roy.

DOCTORAL EXAMINATION AND DISSERTATION REPORT

Candidate: Minwen Liu

Major Field: Civil Engineering

Title of Dissertation: Mobilization of a Hydrophobic Organic Compound Using Surfactant for Soil Washing

Approved:

Dibyan Roy
Major Professor and Chairman

Dean of the Graduate School

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Date of Examination:

July 2, 1993